PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of
Toshiaki AOAI, *et al.*
Appln. No.: 09/620,708 Group Art Unit: 1752
Filed: July 20, 2000 Examiner: Chu, John S Y
For: POSITIVE PHOTORESIST COMPOSITION FOR FAR ULTRAVIOLET EXPOSURE

STATEMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir/Madam:

I, Yukio KAWAHARA, residing at Center Hill D-804, 5, Nokendai-Higashi, Kanazawa-ku, Yokohama-City, Kanagawa, Japan, hereby state that:

I well understand the Japanese and English languages and attached is an accurate English translation made by me of Japanese Patent Application No. Hei. 11-207958, filed July 22, 1999.

Date : August 20, 2002 Name : ____________
Yukio KAWAHARA

[Name of document] Specification

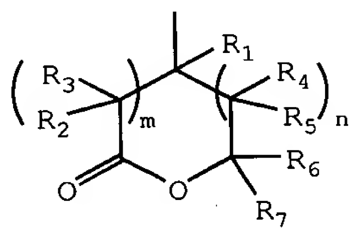
[Title of the Invention] POSITIVE PHOTORESIST COMPOSITION

[Claim]

1. A positive photoresist composition comprising:

(A) a compound capable of generating an acid upon irradiation with actinic rays or radiation and

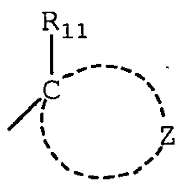
(B) a resin capable of decomposing under the action of an acid to increase the solubility in alkali, containing a repeating unit having a group represented by the following formula (I):



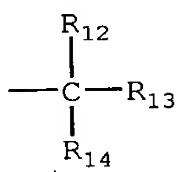
(I)

wherein R_1 represents hydrogen atom or an alkyl group having from 1 to 4 carbon atoms, which may have a substituent, R_2 to R_7, which may be the same or different, each represents hydrogen atom, an alkyl group which may have a substituent, a cycloalkyl group which may have a substituent or an alkenyl group which may have a substituent, provided that at least one of R_6 and R_7 is a group exclusive of hydrogen atom and R_6 and R_7 may combine to form a ring, and m and n each independently represents 0 or 1, provided that m and n are not 0 at the same time.

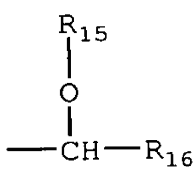
2. The positive photoresist composition as claimed in claim 1, wherein the resin (B) further contains a repeating unit having an alkali-soluble group protected by at least one group containing an alicyclic hydrocarbon structure represented by the following formula (pI), (pII), (pIII), (pIV), (pV) or (pVI):



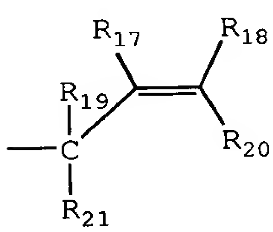
(pI)



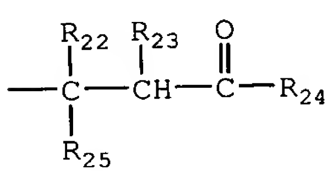
(pII)



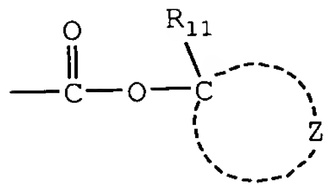
(pIII)



(pIV)



(pV)

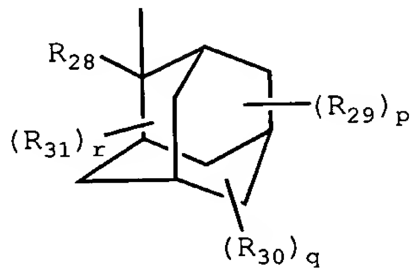


(pVI)

wherein R_{11} represents a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group or a sec-butyl group; Z represents an atomic group necessary for forming an alicyclic hydrocarbon group together with the carbon atom; R_{12} to R_{16} each independently represents a linear or branched alkyl group having from 1 to 4 carbon atoms or an alicyclic hydrocarbon group, provided that at least one of R_{12} to R_{14} or either one of R_{15} and R_{16} represents an alicyclic hydrocarbon group; R_{17} to R_{21} each independently represents hydrogen atom, a linear or branched alkyl group having from 1 to 4 carbon atoms or an alicyclic hydrocarbon group, provided that at least one of R_{17} to R_{21} represents an alicyclic hydrocarbon group and either one of R_{19} and R_{21} represents a linear or branched alkyl group having from 1 to 4 carbon atoms or an alicyclic hydrocarbon group; and R_{22} to R_{25} each independently represents a linear or branched alkyl group having from 1 to 4 carbon atoms or an alicyclic hydrocarbon group, provided that at least one of R_{22} to R_{25} represents an alicyclic hydrocarbon group.

3. The positive photoresist composition as claimed

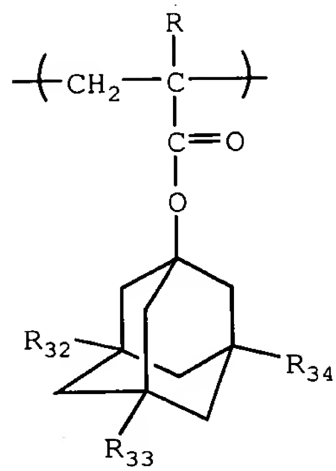
in claim 2, wherein the group containing an alicyclic hydrocarbon structure represented by formula (pI), (pII), (pIII), (pIV), (pV) or (pVI) is a group represented by the following formula (II):



(II)

wherein R_{28} represents an alkyl group which may have a substituent, R_{29} to R_{31}, which may be the same or different, each represents a hydroxy group, a halogen atom, a carboxy group, an alkyl group which may have a substituent, a cycloalkyl group which may have a substituent, an alkenyl group which may have a substituent, an alkoxy group which may have a substituent, an alkoxycarbonyl group which may have a substituent or an acyl group which may have a substituent, and p, q and r each independently represents 0 or an integer of 1 to 3.

4. The positive photoresist composition as claimed in any one of claims 1 to 3, wherein the resin (B) contains a repeating unit represented by the following formula (a):



(a)

wherein R represents hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group having from 1 to 4 carbon atoms, and R_{32} to R_{34}, which may be the same or different, each represents hydrogen atom or a hydroxyl group, provided that at least one of R_{32} to R_{34} represents a hydroxyl group.

5. The positive photoresist composition as claimed in any one of claims 1 to 4, which further contains (C) an acid diffusion inhibitor.

6. The positive photoresist composition as claimed in any one of claims 1 to 5, wherein the compound (A) is a sulfonic acid salt compound of sulfonium or iodonium.

7. The positive photoresist composition as claimed in any one of claims 1 to 5, wherein the compound (A) is a sulfonate compound of N-hydroxyimide or a disulfonyldiazomethane compound.

8. The positive photoresist composition as claimed in any one of claims 1 to 7, wherein the exposure light used is a far ultraviolet ray at a wavelength of 150 to 220 nm.

[Detailed Explanation of the Invention]

[Technical Field to which the Invention belongs]

The present invention relates to a positive photoresist composition for use in the ultramicro-lithography process such as production of VLSI (Very Large Scale Integration) and high-capacitance micro-chip and other photofabrication processes. More specifically, the present invention relates to a positive photoresist composition capable of forming a highly precise pattern using light in the far ultraviolet region including an excimer laser ray, particularly, in the region of 250 nm or less.

[Prior Art]

In recent years, the integration degree of integrated circuits is more and more elevated and in the production of a semiconductor substrate such as VLSI, an ultrafine pattern consisting of lines having a width of half micron or less must be worked. To meet this requirement, the wavelength used in the exposure apparatus for photo-lithography increasingly becomes shorter and at the present

time, studies are being made on the use of an excimer laser ray (e.g., XeCl, KrF, ArF) having a short wavelength among far ultraviolet rays.

In the formation of a pattern for lithography using this wavelength region, a chemical amplification-system resist is used.

The chemical amplification-system resist in general can be roughly classified into three groups, that is, commonly called 2-component system, 2.5-component system and 3-component system. The 2-component system uses a combination of a compound capable of generating an acid by the photochemical decomposition (hereinafter referred to as a "photo-acid generator") and a binder resin. This binder resin is a resin having within the molecule thereof a group capable of decomposing under the action of an acid and thereby increasing solubility of the resin in an alkali developer (also called acid-decomposable group). The 2.5-component system contains a low-molecular weight compound having an acid-decomposable group in addition to the 2-component system. The 3-component system contains a photo-acid generator, an alkali-soluble resin and the above-described low-molecular weight compound.

The chemical amplification-system resist is suitable as a photoresist for use under irradiation with an

ultraviolet ray or a far ultraviolet ray but still in need of coping with the characteristics required on use. For example, a resist composition using a polymer obtained by introducing an acetal or ketal protective group into a hydroxystyrene-base polymer which exhibits small light absorption particularly for light at 248 nm of a KrF excimer laser has been proposed in JP-A-2-141636 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-2-19847, JP-A-4-219757, JP-A-5-281745 and the like. In addition, a similar composition using a t-butoxycarbonyloxy or p-tetrahydro-pyranyloxy group as the acid-decomposable group has been proposed in JP-A-2-209977, JP-A-3-206458 and JP-A-2-19847.

These compositions are suitable for the case of using light at 248 nm of the KrF excimer laser, however, when an ArF excimer laser is used as the light source, the substantial absorbance is still excessively large and therefore, the sensitivity is low. Accompanying this, other problems arise, such as deterioration in the resolution, the focus allowance or the pattern profile. Thus, improvements are necessary in many points.

As a photoresist composition for use with an ArF light source, a resin in which an alicyclic hydrocarbon site is introduced so as to impart dry etching resistance has been

proposed. Examples of this resin include resins obtained by copolymerizing a monomer having a carboxylic acid site such as acrylic acid or methacrylic acid or a monomer having a hydroxyl group or a cyano group within the molecule, with a monomer having an alicyclic hydrocarbon group.

Other than the above-described method of introducing an alicyclic hydrocarbon site into the side chain of an acrylate-base monomer, a method of using an alicyclic hydrocarbon site in the polymer main chain to impart dry etching resistance is also being studied.

Furthermore, JP-A-9-73173, JP-A-9-90637 and JP-A-10-161313 describe a resist material using an acid-sensitive compound containing an alkali-soluble group protected by a structure containing an alicyclic group, and a structural unit for allowing the alkali-soluble group to be released under the action of an acid and render the compound alkali-soluble.

In addition, a resin obtained by introducing a hydrophilic 5- or 6-membered ring lactone group into the above-described resin having an alicyclic group so as to improve the affinity for an alkali developer or the adhesion to a substrate is described in JP-A-9-90637, JP-A-10-207069, JP-A-10-274852 and JP-A-10-239846.

However, these techniques are insufficient for

photoresist compositions (particularly photoresist compositions for far ultraviolet exposure) in many points resulting from the resin containing an acid-decomposable group, for example, improvements for higher sensitivity and higher resolution or improvement of the adhesive property to a substrate caused by containing an aliphatic cyclic hydrocarbon group in the molecule, and they are still in need of improvements.

Also, in recent years, to cope with the requirement for semiconductor chips in a finer size, the design pattern for the fine semiconductor has reached to a region as fine as 0.13 to 0.35 μm. The above-described compositions have, however, a problem in that the resolution of the pattern is inhibited due to the factors such as edge roughness of the line pattern or the like. The term "edge roughness" as used herein means the fact that due to the properties of the resist, the edges at the top and bottom of a resist line pattern irregularly fluctuate in the direction perpendicular to the line direction and unevenness is observed on the edges when viewed from right above.

[Problem to be resolved by the Invention]

Thus, conventional photoresist compositions in known arts cannot respond to the recently required performance in the sensitivity, the resolution or the adhesion to a

substrate. Moreover, edge roughness of a pattern is observed and a stable pattern cannot be obtained. Under these circumstances, more improvements are being demanded.

Accordingly, an object of the present invention is to provide a chemical amplification-type positive photoresist composition favored with high sensitivity, high resolution and good adhesion to a substrate and improved in the edge roughness of a pattern.

[Means to resolve the Problem]

As a result of extensive studies on the constituent material of a resist composition in the positive chemical amplification system, the present inventors have found that the objects of the present invention can be attained by using an acid-decomposable resin having a specific lactone structure. The present invention has been accomplished based on this finding.

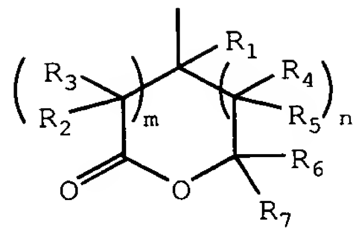
More specifically, the objects of the present invention can be attained by the following constructions.

(1) A positive photoresist composition comprising:

(A) a compound capable of generating an acid upon irradiation with actinic rays or radiation and

(B) a resin capable of decomposing under the action of an acid to increase the solubility in alkali, containing a repeating unit having a group represented by the

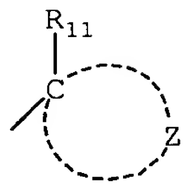
following formula (I):



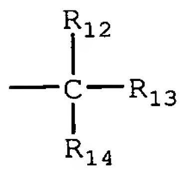
(I)

wherein R_1 represents hydrogen atom or an alkyl group having from 1 to 4 carbon atoms, which may have a substituent, R_2 to R_7, which may be the same or different, each represents hydrogen atom, an alkyl group which may have a substituent, a cycloalkyl group which may have a substituent or an alkenyl group which may have a substituent, provided that at least one of R_6 and R_7 is a group exclusive of hydrogen atom and R_6 and R_7 may combine to form a ring, and m and n each independently represents 0 or 1, provided that m and n are not 0 at the same time.

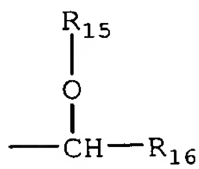
(2) The positive photoresist composition as described in (2) above, wherein the resin (B) further contains a repeating unit having an alkali-soluble group protected by at least one group containing an alicyclic hydrocarbon structure represented by the following formula (pI), (pII), (pIII), (pIV), (pV) or (pVI):



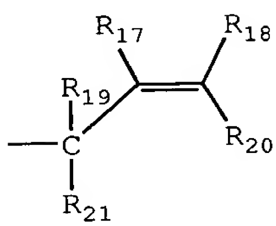
(pI)



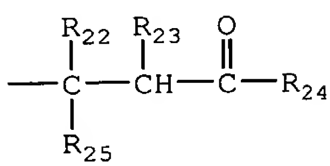
(pII)



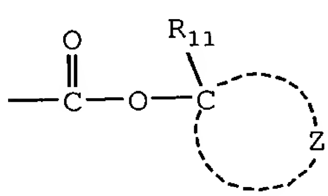
(pIII)



(pIV)



(pV)

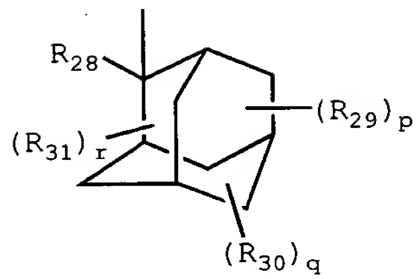


(pVI)

wherein R_{11} represents a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group or a sec-butyl group; Z represents an atomic

group necessary for forming an alicyclic hydrocarbon group together with the carbon atom; R_{12} to R_{16} each independently represents a linear or branched alkyl group having from 1 to 4 carbon atoms or an alicyclic hydrocarbon group, provided that at least one of R_{12} to R_{14} or either one of R_{15} and R_{16} represents an alicyclic hydrocarbon group; R_{17} to R_{21} each independently represents hydrogen atom, a linear or branched alkyl group having from 1 to 4 carbon atoms or an alicyclic hydrocarbon group, provided that at least one of R_{17} to R_{21} represents an alicyclic hydrocarbon group and either one of R_{19} and R_{21} represents a linear or branched alkyl group having from 1 to 4 carbon atoms or an alicyclic hydrocarbon group; and R_{22} to R_{25} each independently represents a linear or branched alkyl group having from 1 to 4 carbon atoms or an alicyclic hydrocarbon group, provided that at least one of R_{22} to R_{25} represents an alicyclic hydrocarbon group.

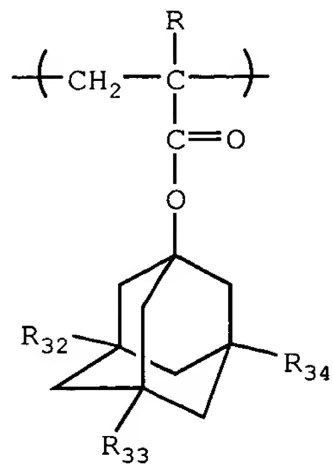
(3) The positive photoresist composition as described in (2) above, wherein the group containing an alicyclic hydrocarbon structure represented by formula (pI), (pII), (pIII), (pIV), (pV) or (pVI) is a group represented by the following formula (II):



(II)

wherein R_{28} represents an alkyl group which may have a substituent, R_{29} to R_{31}, which may be the same or different, each represents a hydroxy group, a halogen atom, a carboxy group, an alkyl group which may have a substituent, a cycloalkyl group which may have a substituent, an alkenyl group which may have a substituent, an alkoxy group which may have a substituent, an alkoxycarbonyl group which may have a substituent or an acyl group which may have a substituent, and p, q and r each independently represents 0 or an integer of 1 to 3.

(4) The positive photoresist composition as described in any one of (1) to (3) above, wherein the resin (B) contains a repeating unit represented by the following formula (a):



(a)

wherein R represents hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group having from 1 to 4 carbon atoms, and R_{32} to R_{34}, which may be the same or different, each represents hydrogen atom or a hydroxyl group, provided that at least one of R_{32} to R_{34} represents a hydroxyl group.

(5) The positive photoresist composition as described in any one of (1) to (4) above, which further contains (C) an acid diffusion inhibitor.

(6) The positive photoresist composition as described in any one of (1) to (5) above, wherein the compound (A) is a sulfonic acid salt compound of sulfonium or iodonium.

(7) The positive photoresist composition as described in any one of (1) to (5) above, wherein the compound (A) is a sulfonate compound of N-hydroxyimide or a disulfonyldiazomethane compound.

(8) The positive photoresist composition as described in any one of (1) to (7) above, wherein the exposure light used is a far ultraviolet ray at a wavelength of 150 to 220 nm.

[Embodiment of the Invention]

The compounds for use in the present invention are descried in detail below.

(A) Compound Capable of Generating Acid Upon Irradiation with Actinic Rays or Radiation (Photo-Acid Generator)

The photo-acid generator (A) for use in the present invention is a compound which generates an acid upon irradiation with actinic rays or radiation.

Examples of the photo-acid generator for use in the present invention include a photocationic polymerization initiator, a photoradical polymerization initiator, a photo-decoloring agent for dyes, a photo-discoloring agent and a compound capable of generating an acid upon irradiation with a known ray used for microresist or the like (for example, ultraviolet or far ultraviolet ray of 200 to 400 nm, preferably g-line, h-line, i-line and KrF excimer laser ray), an ArF excimer laser ray, an electron beam, an X ray, a molecular beam or an ion beam. These may be appropriately selected and used either individually or in combination.

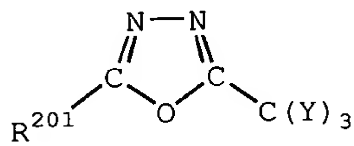
Other examples of the photo-acid generator for use in the present invention include onium salts such as diazonium salt, ammonium salt, phosphonium salt, iodonium salt, sulfonium salt, selenonium salt and arsonium salt; organic halogen compounds; organic metals/organic halides; photo-acid generators having an o-nitrobenzyl type protective group; compounds capable of photochemically decomposing to generate a sulfonic acid, such as iminosulfonate; disulfone compounds; diazoketosulfone; and diazosulfone compounds.

In addition, compounds obtained by introducing the above-described group or compound capable of generating an acid upon irradiation with light into the main chain or a side chain of a polymer may also be used.

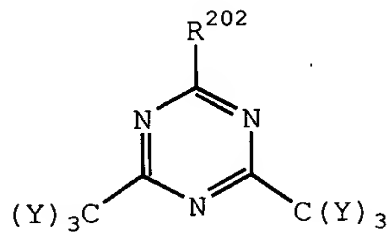
Furthermore, compounds capable of generating an acid upon irradiation of light described in V.N.R. Pillai, Synthesis, (1), 1 (1980), A. Abad et al., Tetrahedron Lett., (47) 4555 (1971), D.H.R. Barton et al., J. Chem. Soc., (C), 329 (1970), U.S. Patent 3,779,778, European Patent 126,712 and the like may also be used.

Out of these compounds capable of decomposing upon irradiation with actinic rays or radiation and thereby generating an acid, particularly effective compounds are described below.

(1) Oxazole Derivative Represented by Formula (PAG1) and S-Triazine Derivative Represented by Formula (PAG2), Each Substituted by Trihalomethyl Group:



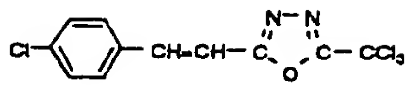
(PAG1)



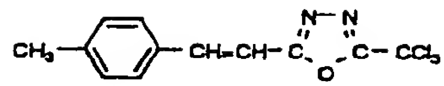
(PAG2)

wherein R^{201} represents a substituted or unsubstituted aryl group or a substituted or unsubstituted alkenyl group, R^{202} represents a substituted or unsubstituted aryl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkyl group or $-C(Y)_3$, and Y represents chlorine atom or bromine atom.

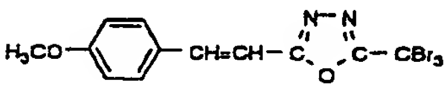
Specific examples thereof include the following compounds, however, the present invention is by no means limited thereto.



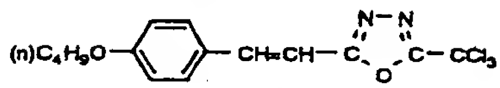
(PAG1-1)



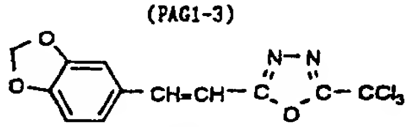
(PAG1-2)



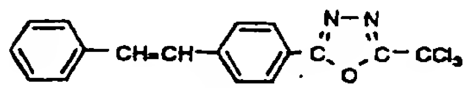
(PAG1-3)



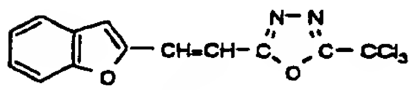
(PAG1-4)



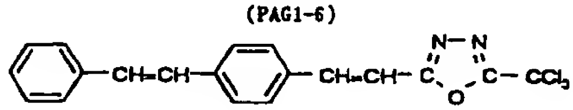
(PAG1-5)



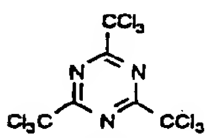
(PAG1-6)



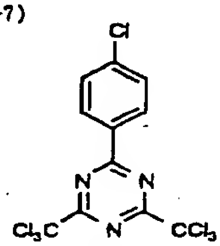
(PAG1-7)



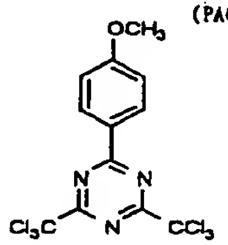
(PAG1-8)



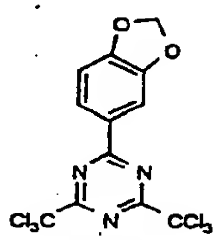
(PAG2-1)



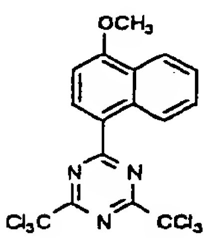
(PAG2-2)



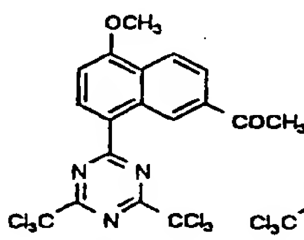
(PAG2-3)



(PAG2-4)



(PAG2-5)



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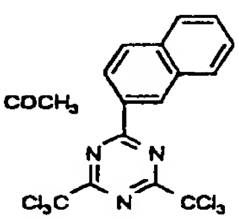

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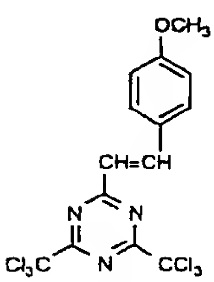

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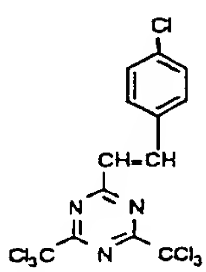

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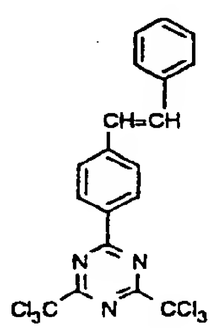
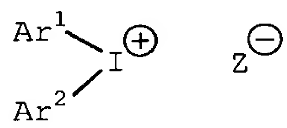
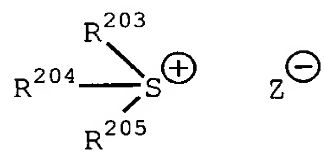


(PAG2-10)

(2) Iodonium Salt Represented by Formula (PAG3) and Sulfonium Salt Represented by Formula (PAG4):



(PAG3)



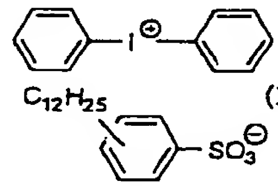
(PAG4)

wherein Ar^1 and Ar^2 each independently represents a substituted or unsubstituted aryl group, R^{203}, R^{204} and R^{205} each independently represents a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group,

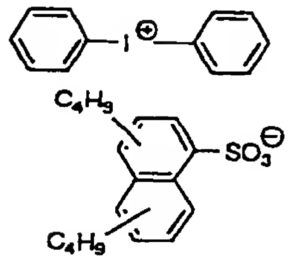
Z^- represents a counter anion and examples thereof include BF_4^-, AsF_6^-, PF_6^-, SbF_6^-, SiF_6^{2-}, ClO_4^-, perfluoroalkane sulfonate anion such as $CF_3SO_3^-$, toluenesulfonate anion, substituted benzenesulfonate anion such as dodecylbenzenesulfonate anion and pentafluorobenzenesulfonate anion, condensed polynuclear aromatic sulfonate anion such as naphthalene-1-sulfonate anion and anthraquinonesulfonate anion, and sulfonic acid group-containing dye, but the present invention is by no means limited thereto.

Two of R^{203}, R^{204} and R^{205}, and Ar^1 and Ar^2 in respective pairs may be bonded through a single bond or a substituent.

Specific examples thereof include the following compounds, however, the present invention is by no means limited thereto.



(PAG3-1)



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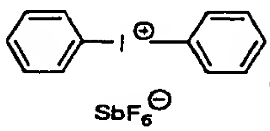

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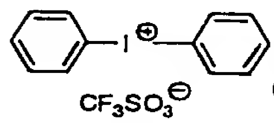

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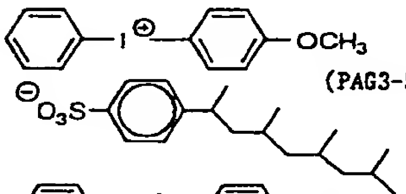

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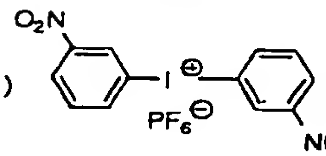

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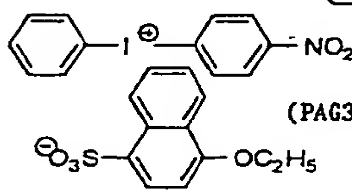

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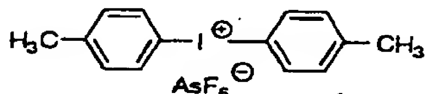

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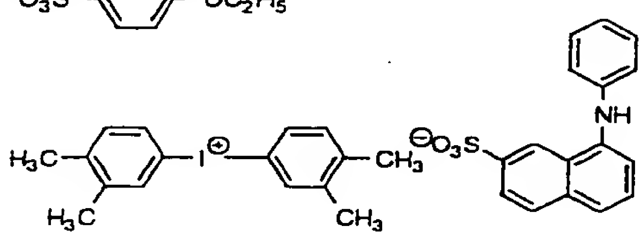

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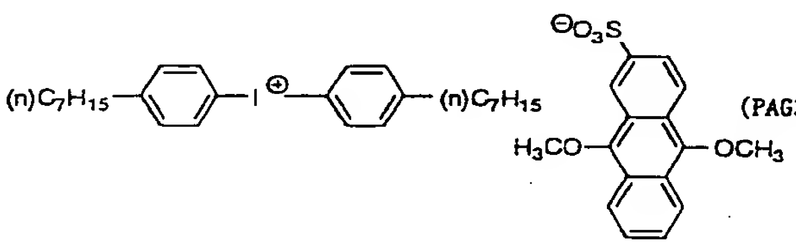

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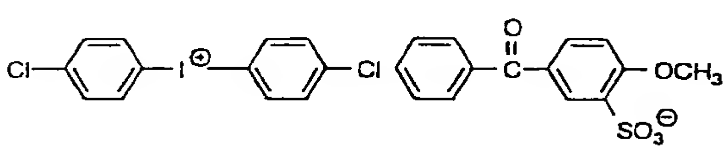

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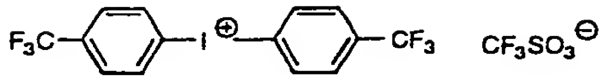
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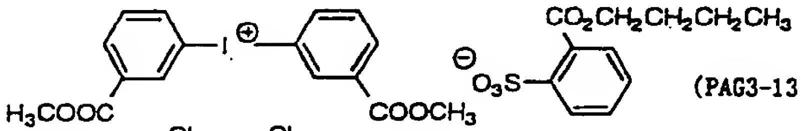
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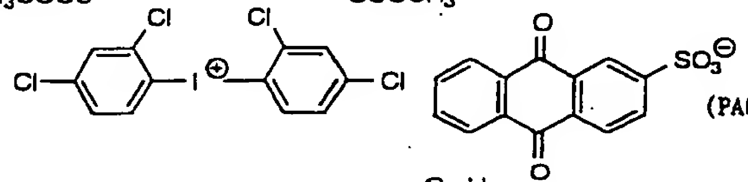
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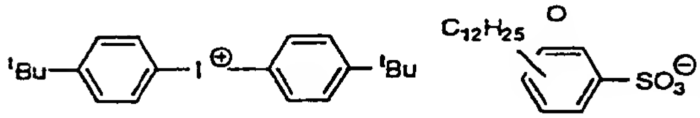
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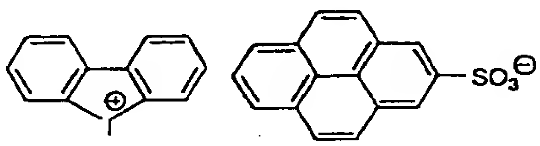
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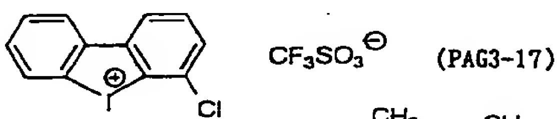
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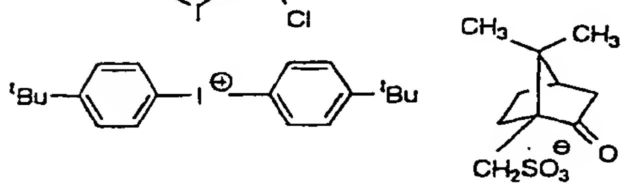
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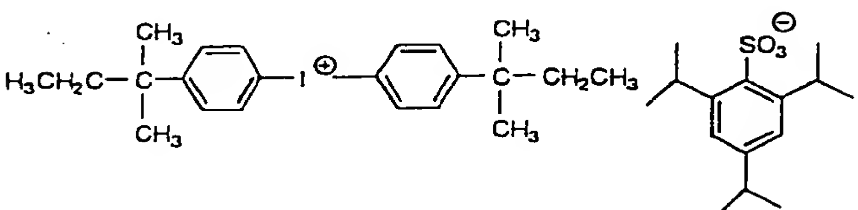
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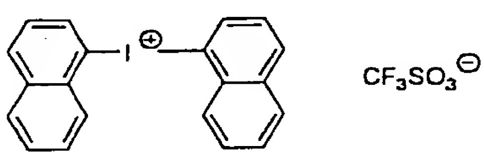
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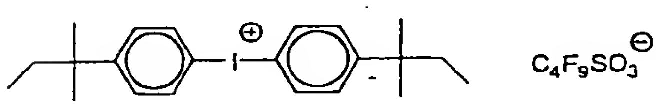
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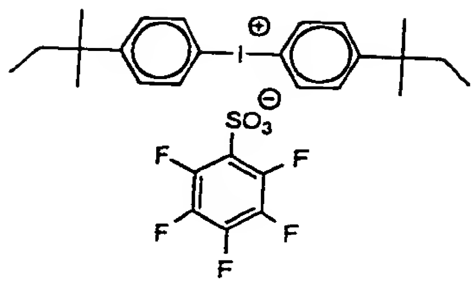

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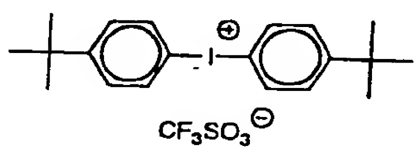

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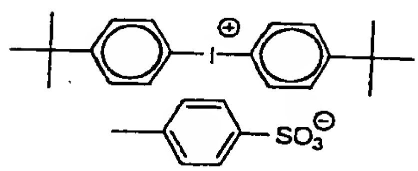

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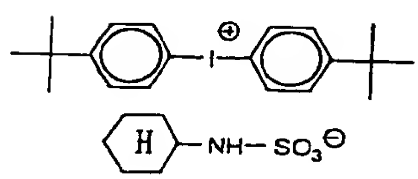

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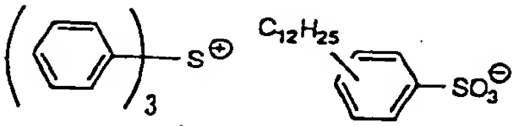

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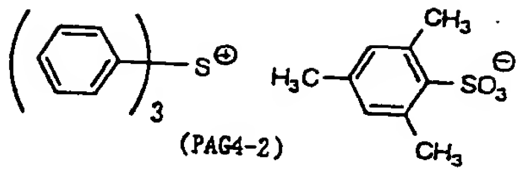

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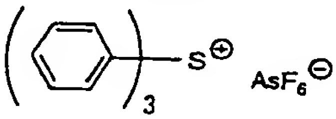

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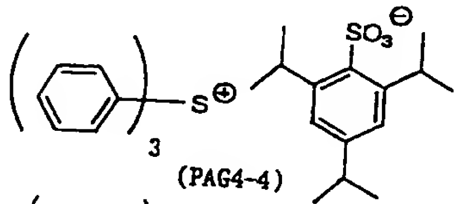

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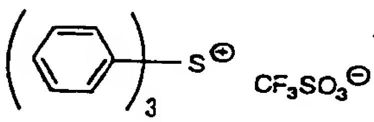

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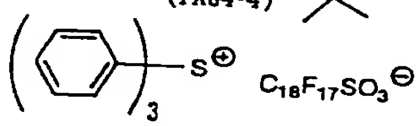

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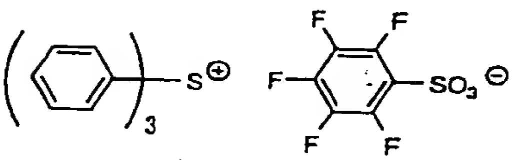

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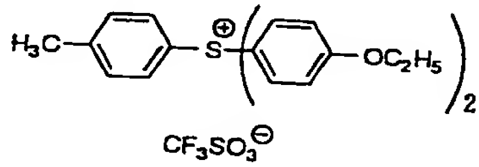

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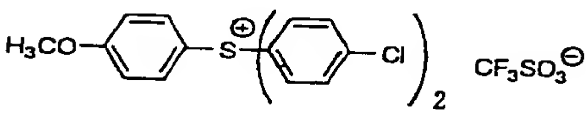

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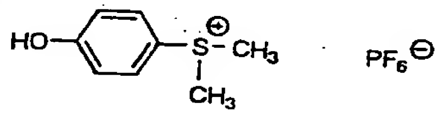

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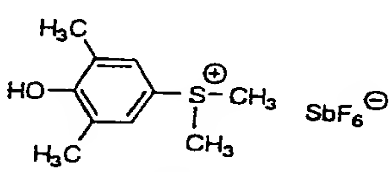

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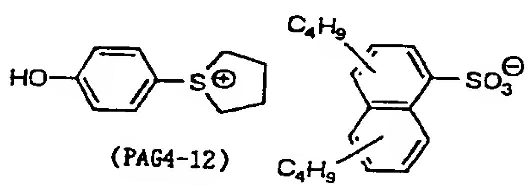

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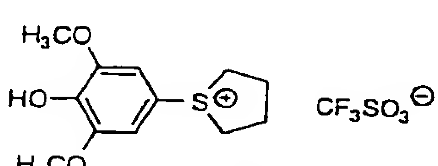

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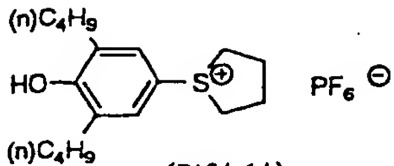

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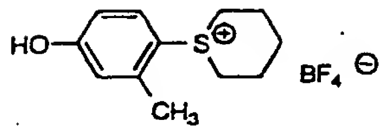

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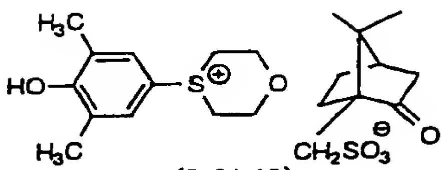

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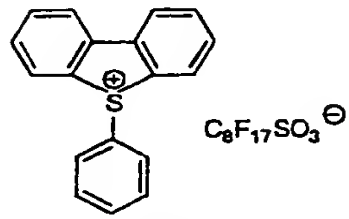

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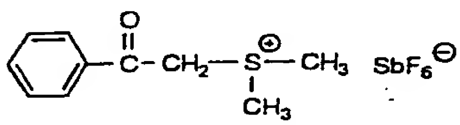

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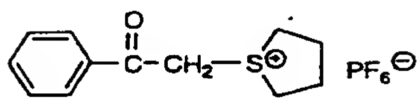

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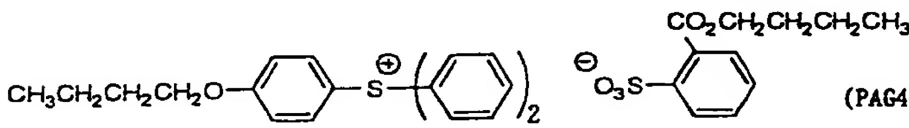

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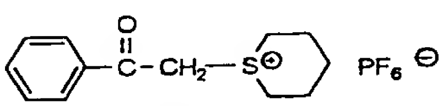

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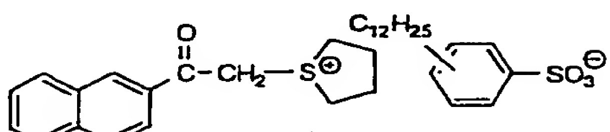

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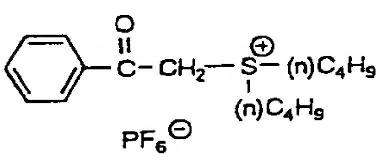

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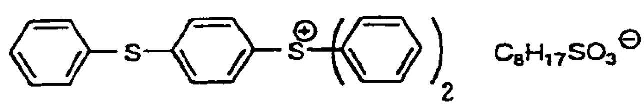

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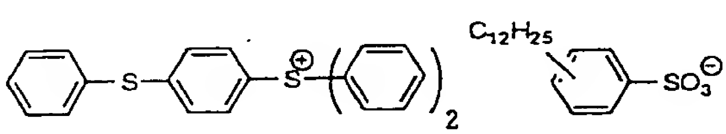

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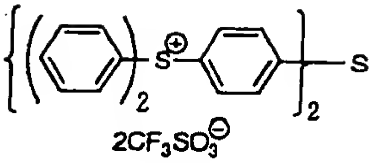

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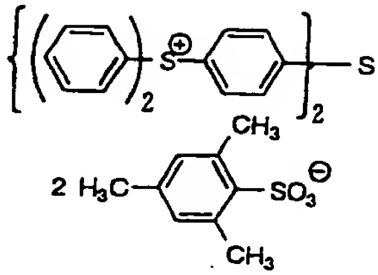

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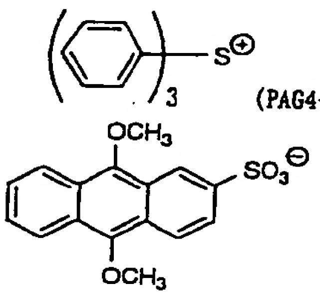

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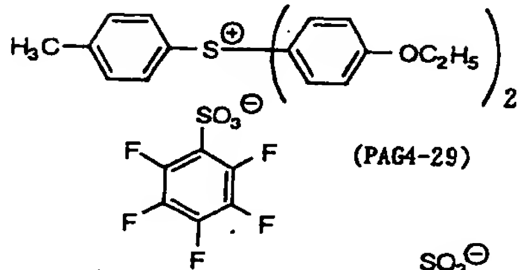

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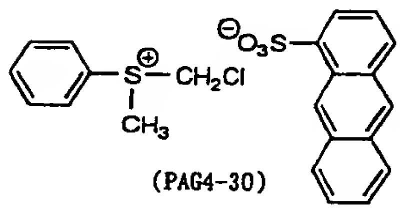

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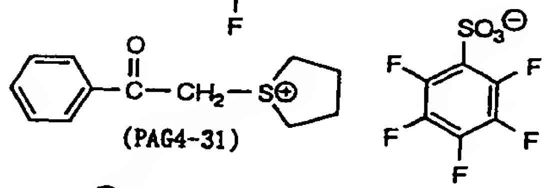

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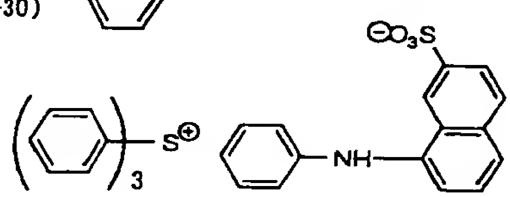

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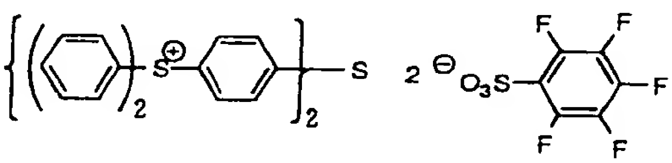

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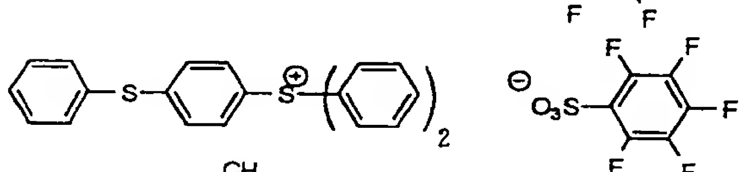

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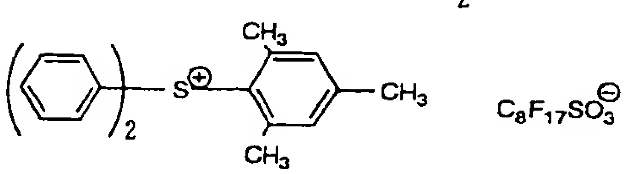
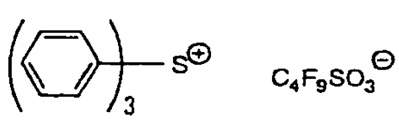
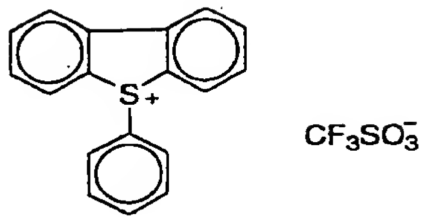


(PAG4-35)



(PAG4-36)

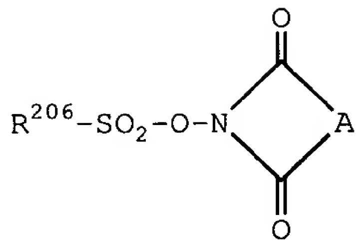
PAG4-37



The above-mentioned onium salts represented by formulae (PAG3) and (PAG4) are known and may be synthesized by a method described, for example, in J.W. Knapczyl et al., J. Am. Chem. Soc., 91, 145 (1969), A.L. Maycok et al., J. Org. Chem., 35, 2532 (1970), E. Goethas et al., Bull. Soc. Chem. Belg., 73, 546 (1964), H.M. Leicester, J. Am. Chem. Soc., 51, 3587 (1929), J.V. Crivello et al., J. Polym. Chem. Ed., 18, 2677 (1980), U.S. Patents 2,807,648 and 4,247,473, JP-A-53-101331.

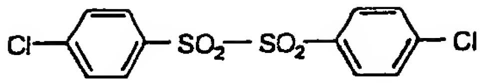
(3) Disulfonic Acid Derivative Represented by Formula (PAG5) and Imidosulfonate Derivative Represented by Formula (PAG6):

$$Ar^3\text{-}SO_2\text{-}SO_2\text{-}Ar^4 \qquad \text{(PAG5)}$$

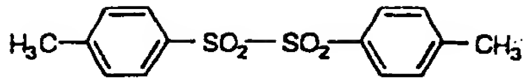
 (PAG6)

wherein Ar^3 and Ar^4 each independently represents a substituted or unsubstituted aryl group, R^{206} represents a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group, and A represents a substituted or unsubstituted alkylene group, a substituted or unsubstituted alkenylene group or a substituted or unsubstituted arylene group.

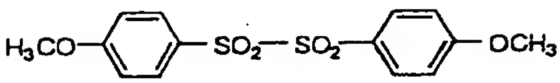
Specific examples thereof include the following compounds, however, the present invention is by no means limited thereto.



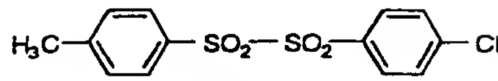
(PAG5-1)



(PAG5-2)



(PAG5-3)



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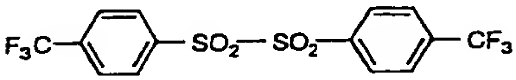

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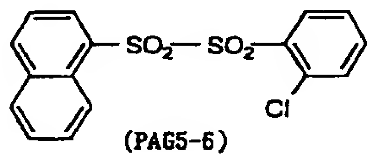

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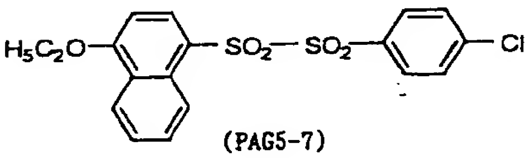

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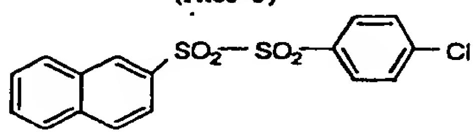

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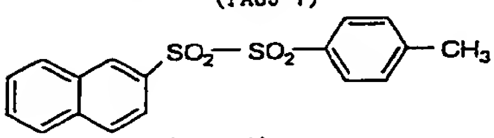

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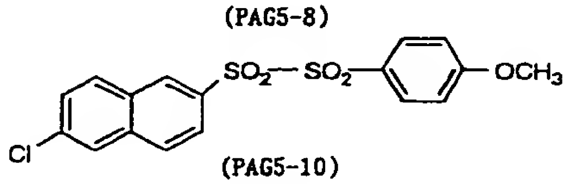

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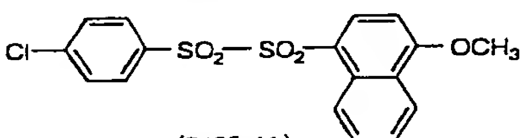

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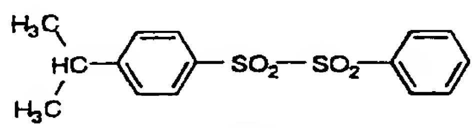

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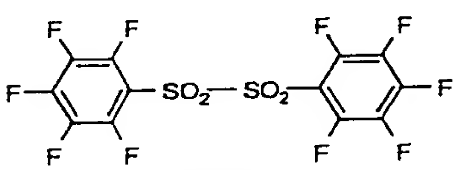

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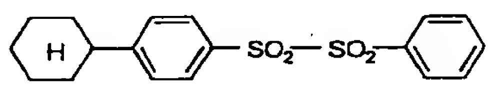

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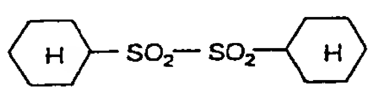

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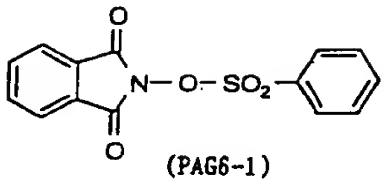
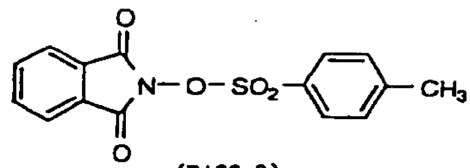


(PAG6-1)



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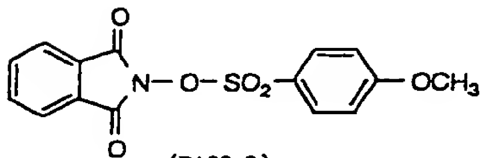

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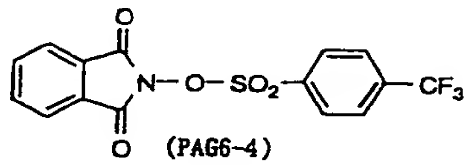

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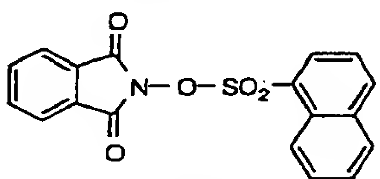

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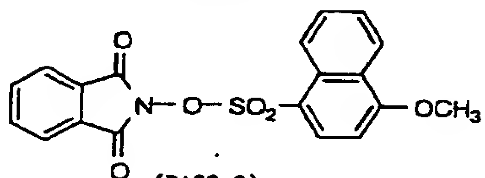

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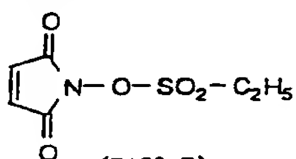

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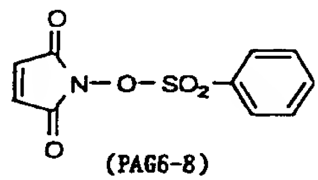

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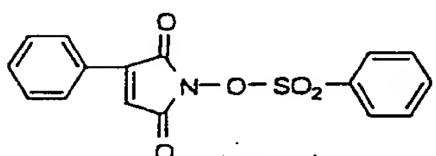

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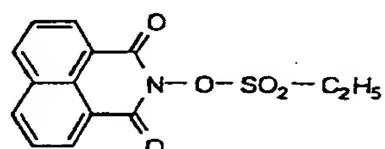
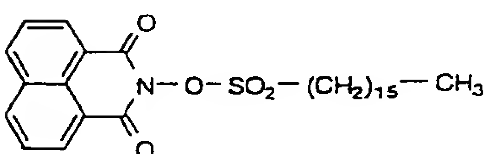
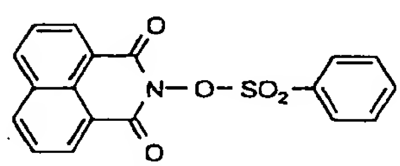


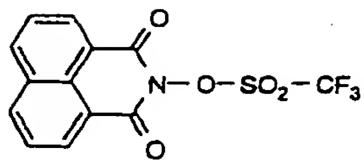
(PAG6-10)



(PAG6-11)



(PAG6-12)



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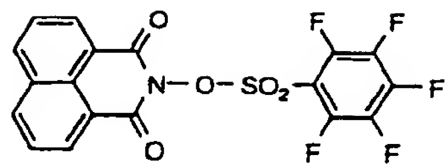
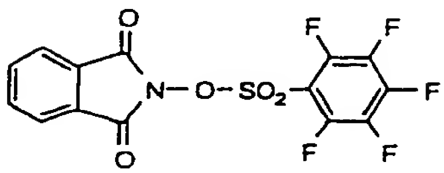


(PAG6-14)



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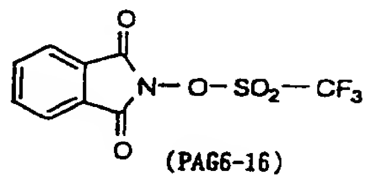
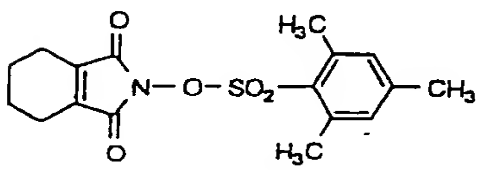


(PAG6-16)



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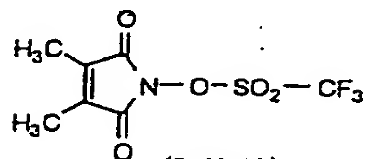
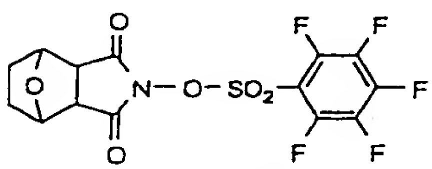
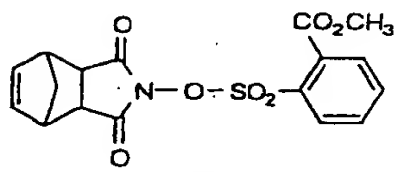


(PAG6-18)

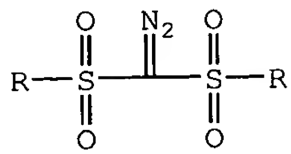


(PAG6-19)



(PAG6-20)

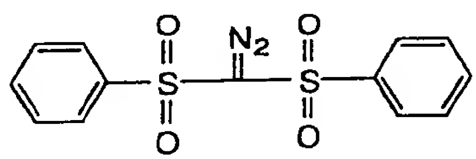
(4) Diazodisulfone Derivative Represented by Formula (PAG7)



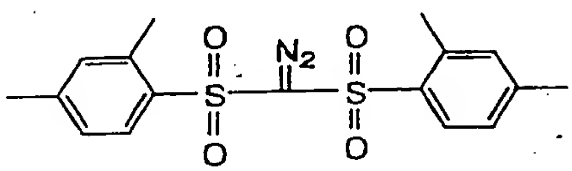
(PAG7)

wherein R represents a linear, branched or cyclic alkyl group or an aryl group which may be substituted.

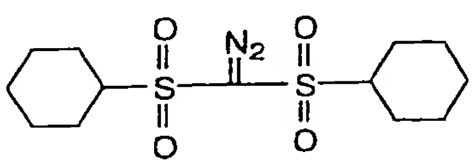
Specific examples thereof include the following compounds, however, the present invention is not limited thereto.



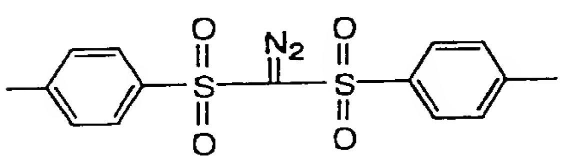
(PAG7-1)



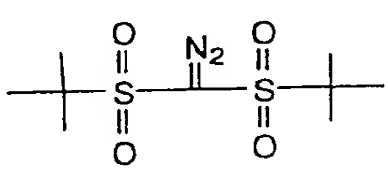
(PAG7-2)



(PAG7-3)



(PAG7-4)



(PAG7-5)

In the present invention, the photo-acid generator is preferably a sulfonic acid salt compound of sulfonium or iodonium (more preferably a compound represented by formula (PAG3) or (PAG4)), a sulfonate compound of N-hydroxyimide (more preferably a compound represented by formula (PAG6)) or a disulfonyldiazomethane compound (more preferably a compound represented by formula (PAG7)). By using such a photo-acid generator, high sensitivity and excellent resolution can be obtained and the fine pattern formed can be highly improved in the edge roughness.

The photo-acid generator is usually added in an amount of, based on the solid content in the composition, 0.001 to 40 wt%, preferably 0.01 to 20 wt%, more preferably 0.1 to 5 wt%. If the amount of the photo-acid generator added is less than 0.001 wt%, the sensitivity decreases, whereas if the added amount exceeds 40 wt%, the resist is excessively increased in the light absorption to disadvantageously cause deterioration of the profile or narrowing of the process (particularly, bake) margin.

(B) Resin Capable of Decomposing Under Action of Acid to Increase Solubility in Alkali

The resin (B) capable of decomposing under the action of an acid to increase the solubility in alkali (hereinafter sometimes simply referred to as a "resin (B)"),

for use in the present invention, contains a repeating unit having a group represented by formula (I).

In formula (I), the alkyl group having from 1 to 4 carbon atoms represented by R_1, which may have a substituent, includes a linear or branched alkyl group having from 1 to 4 carbon atoms. Examples of the alkyl group include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group and a tert-butyl group.

The alkyl group represented by R_2 to R_7 includes a linear or branched alkyl group which may have a substituent. The linear or branched alkyl group is preferably a linear or branched alkyl group having from 1 to 12 carbon atoms, more preferably a linear or branched alkyl group having from 1 to 10 carbon atoms, still more preferably a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, an sec-butyl group, a tert-butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group or a decyl group.

The cycloalkyl group represented by R_2 to R_7 is preferably a cycloalkyl group having from 3 to 8 carbon atoms, such as cyclopropyl group, cyclopentyl group, cyclohexyl group, cycloheptyl group and cyclooctyl group.

The alkenyl group represented by R_2 to R_7 is preferably

an alkenyl group having from 2 to 6 carbon atoms, such as vinyl group, propenyl group, butenyl group and hexenyl group.

Examples of the ring formed as a result of combining of R_6 and R_7 include 3- to 8-membered rings such as cyclopropane ring, cyclobutane ring, cyclopentane ring, cyclohexane ring and cyclooctane ring.

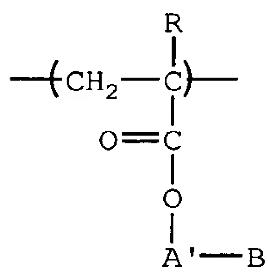
Examples of the substituent of these alkyl group, cycloalkyl group and alkenyl group include an alkoxy group having from 1 to 4 carbon atoms, a halogen atom (e.g., fluorine, chlorine, bromine, iodine), an acyl group, an acyloxy group, a cyano group, a hydroxy group, a carboxy group, an alkoxycarbonyl group and a nitro group.

In the present invention, at least one of R_6 and R_7 is a group exclusive of hydrogen atom, preferably an alkyl group having from 1 to 10 carbon atoms, a cycloalkyl group having 3 to 8 carbon atoms or an alkenyl group having 2 to 6 carbon atoms, more preferably an alkyl group having 1 to 6 carbon atoms.

In the present invention, R_2 to R_4 each is preferably an alkyl group having from 1 to 10 carbon atoms, a cycloalkyl group having from 3 to 8 carbon atoms or an alkenyl group having from 2 to 6 carbon atoms, more preferably an alkyl group having from 1 to 6 carbon atoms.

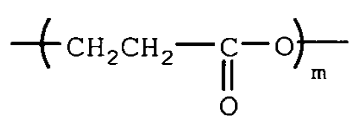
m and n each represents 0 or 1, provided that m and n are not 0 at the same time.

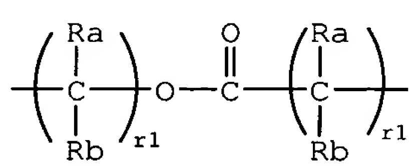
The repeating unit having a group represented by formula (I) is preferably a repeating unit represented by the following formula (AI):

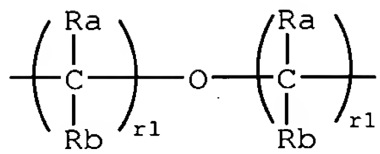


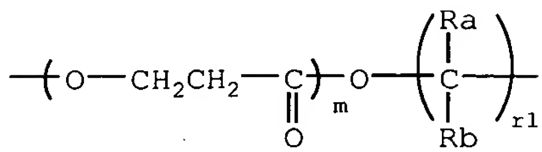
(AI)

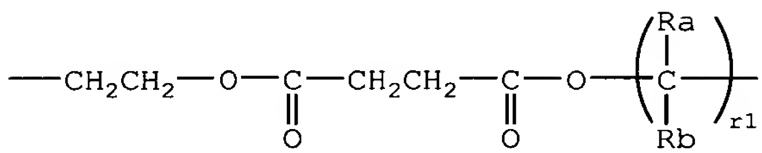
wherein R has the same meaning as R in formula (a) which is described later, A' represents a single bond, an ether group, an ester group, a carbonyl group, an alkylene group or a divalent group comprising a combination thereof, and B represents a group represented by formula (I). Examples of the divalent group comprising the above-described combination, represented by A', include the groups represented by the following formulae:





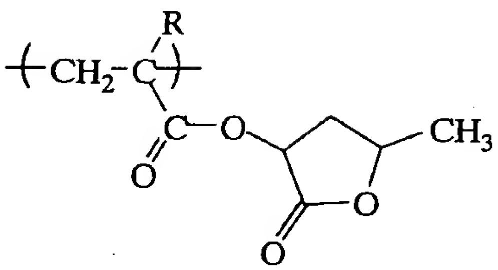




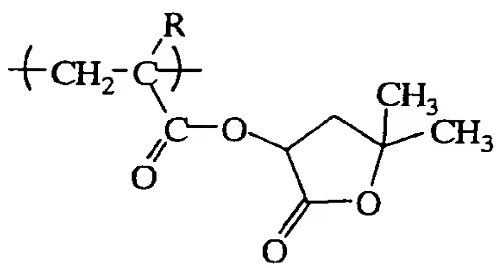


wherein Ra, Rb and r1 have the same meanings as defined later, and m is an integer of 1 to 3.

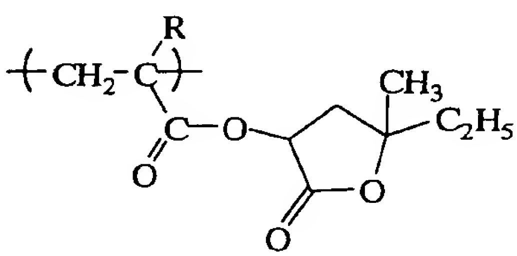
Specific examples of the repeating unit represented by formula (AI) are set forth below, however, the present invention is by no means limited thereto.



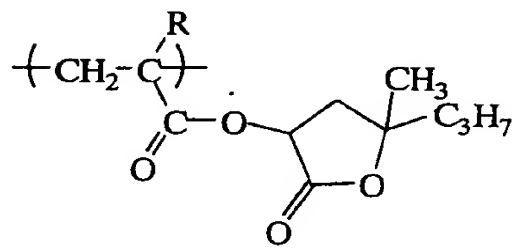
(I-1)



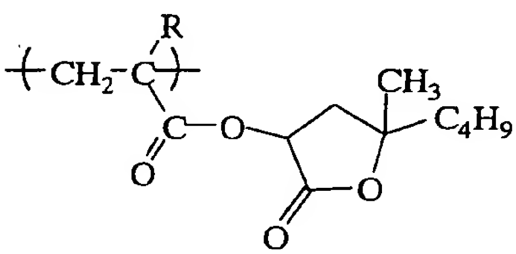
(I-2)



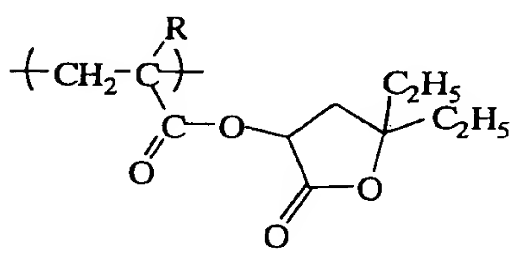
(I-3)



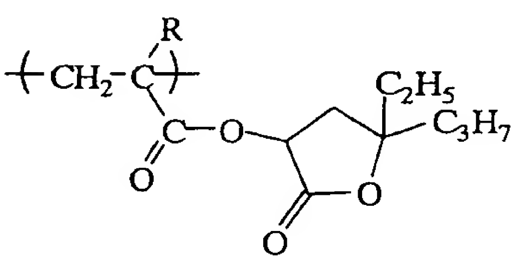
(I-4)



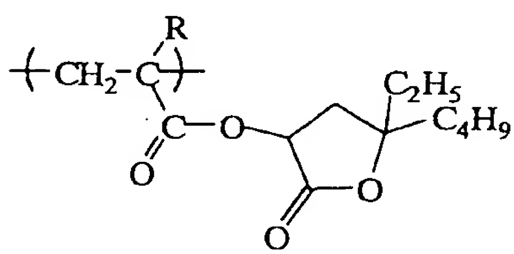
(I-5)



(I-6)



(I-7)



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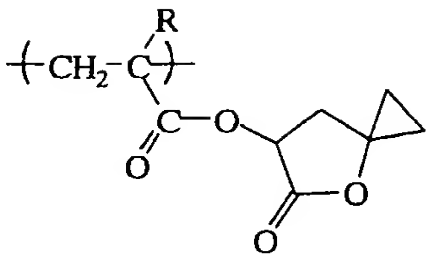

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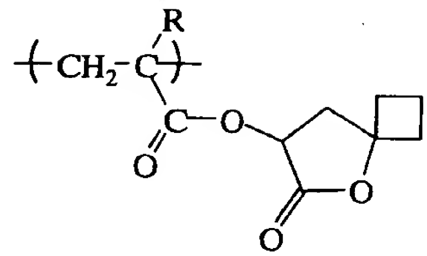

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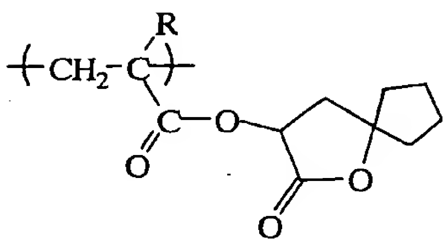

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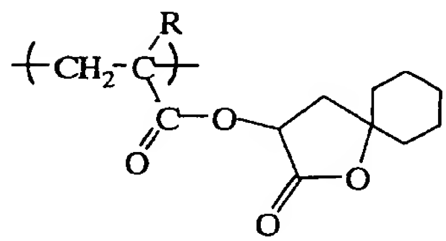

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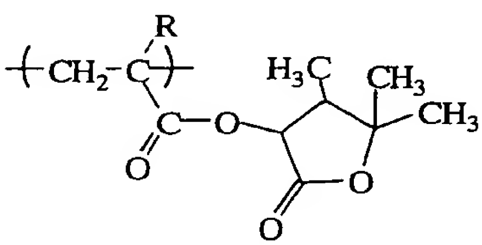

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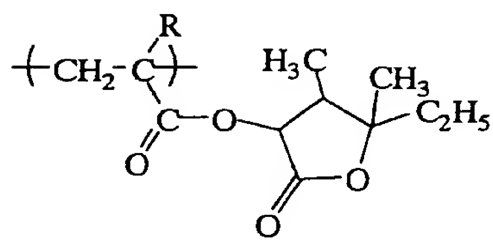

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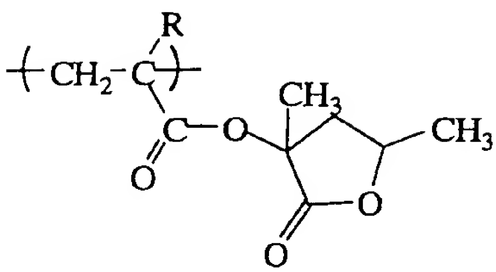

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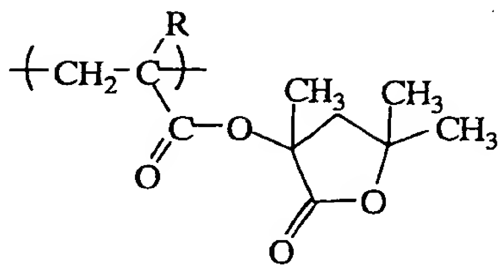

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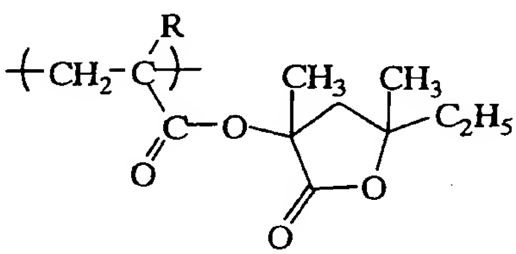

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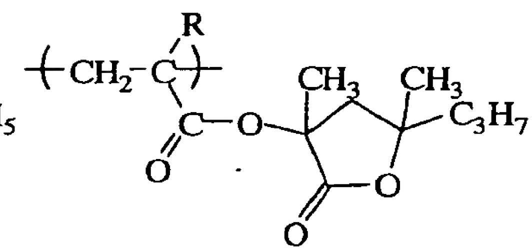

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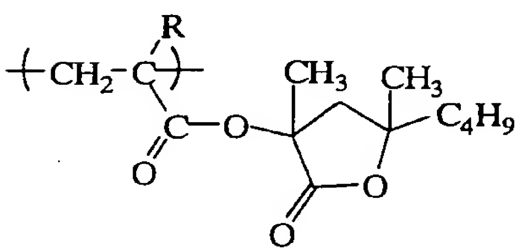

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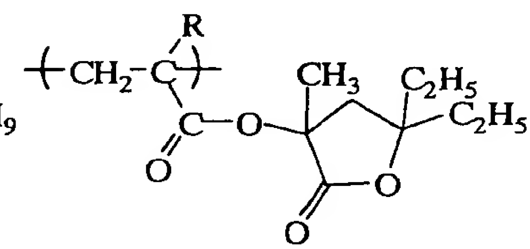

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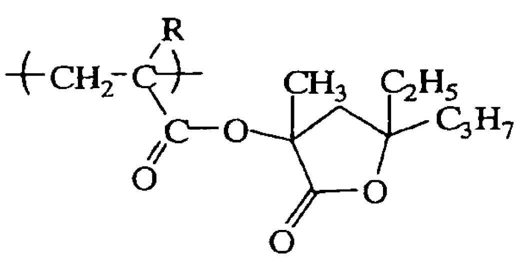

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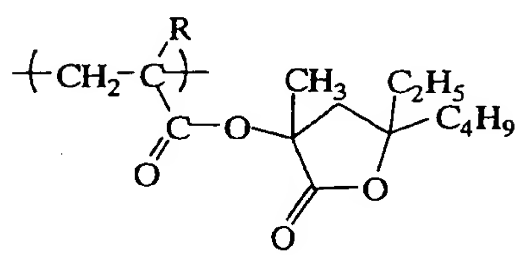

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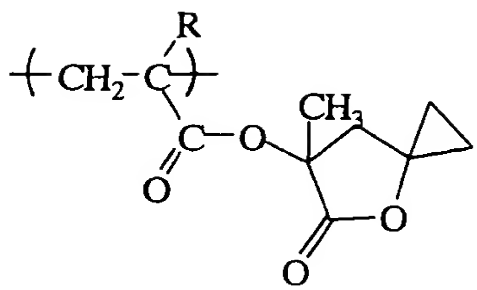

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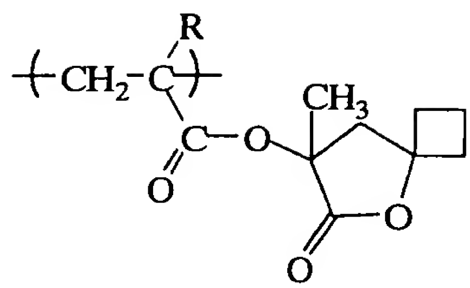

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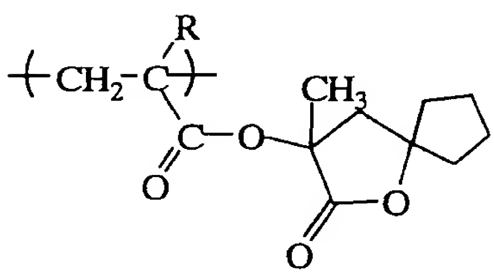

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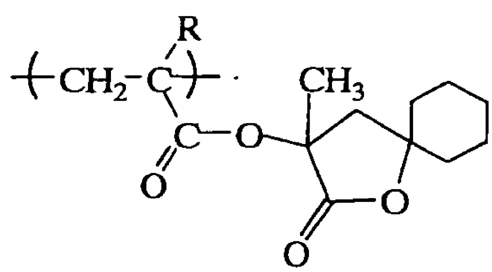

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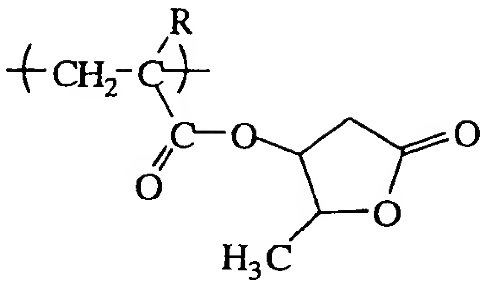

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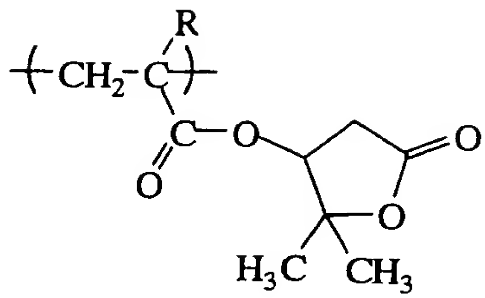

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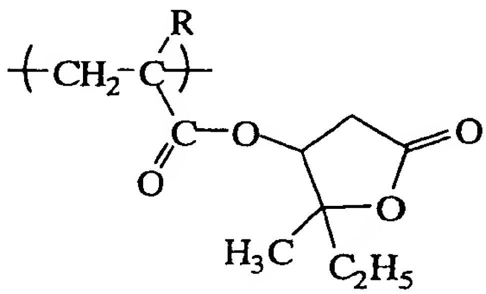

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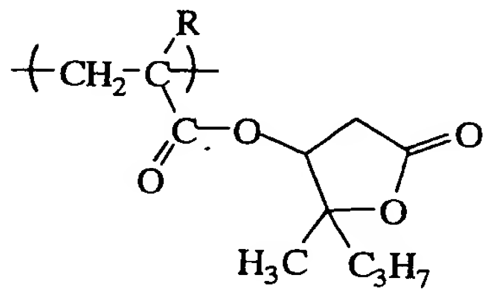

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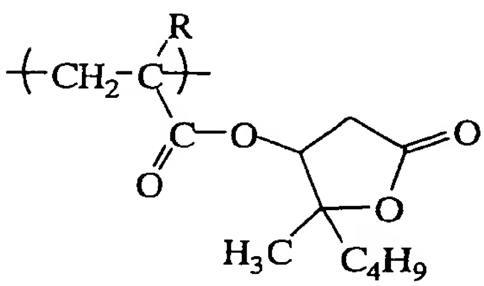

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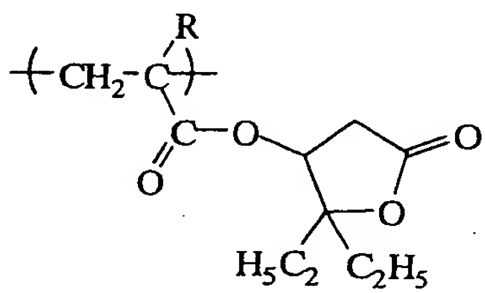

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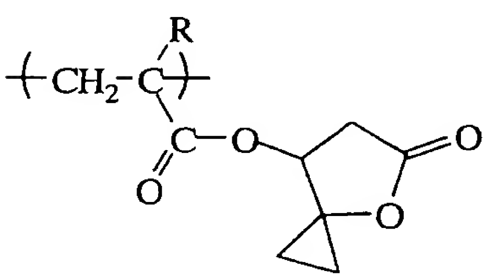

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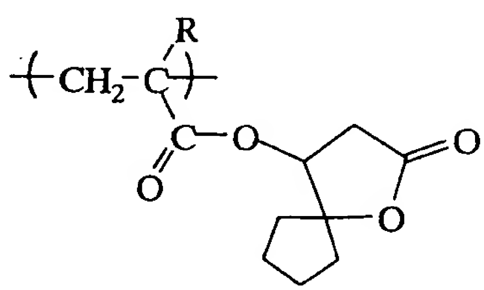

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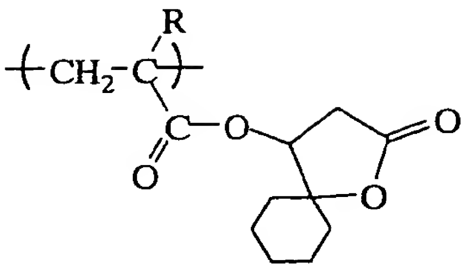

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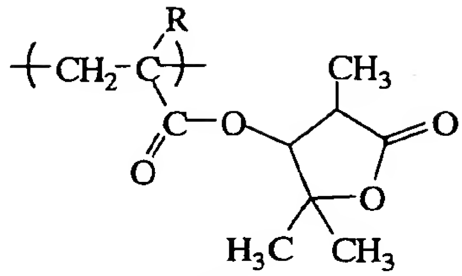

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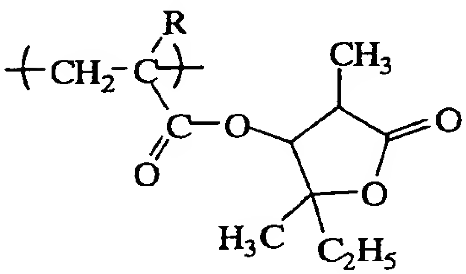

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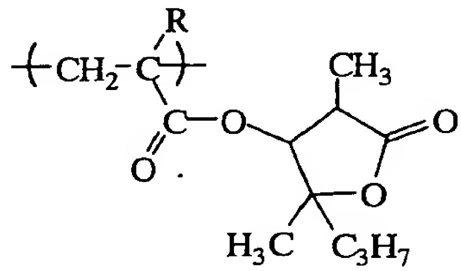

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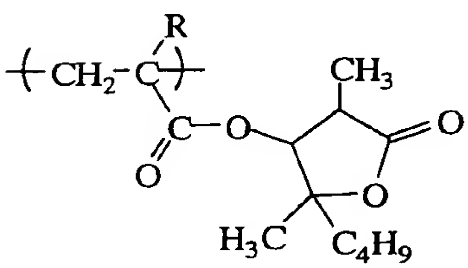

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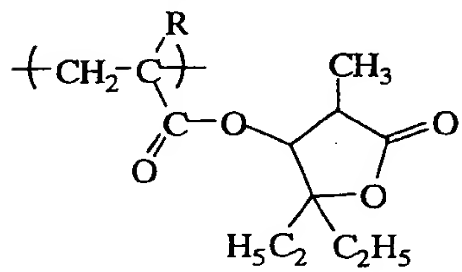

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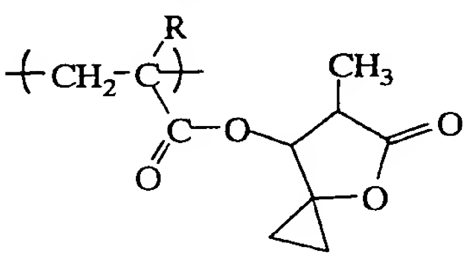

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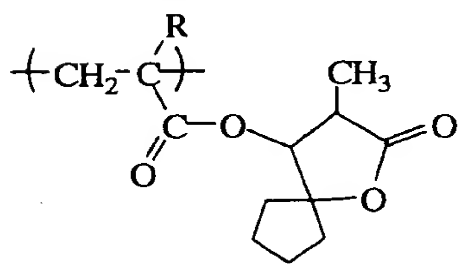

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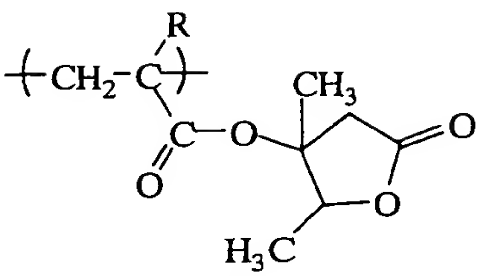

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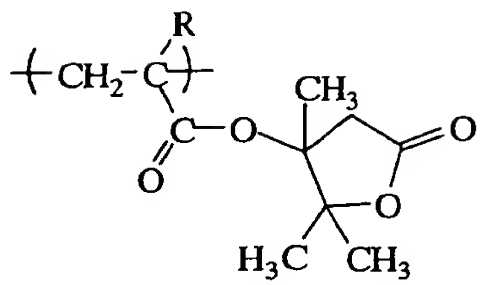

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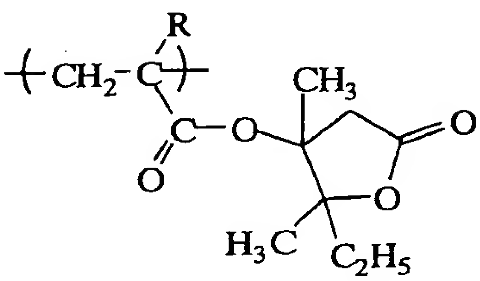

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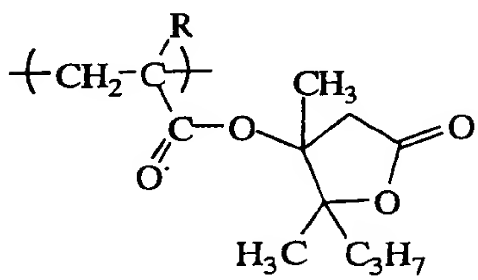

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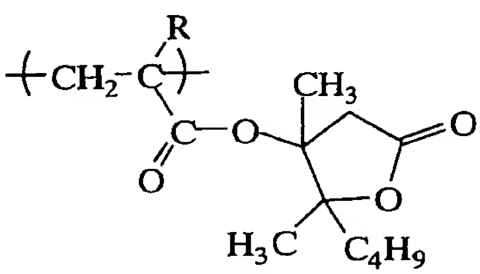

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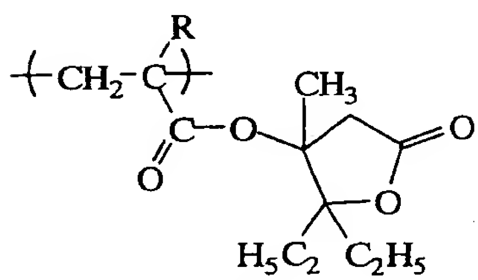

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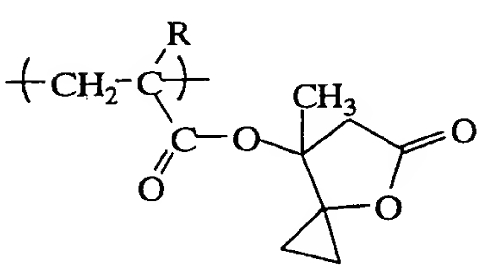

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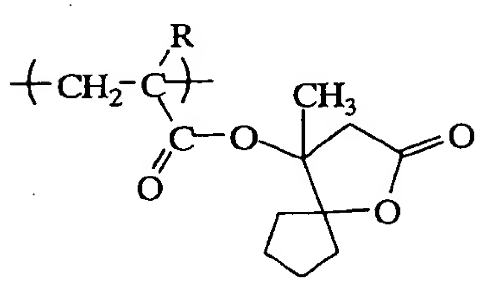

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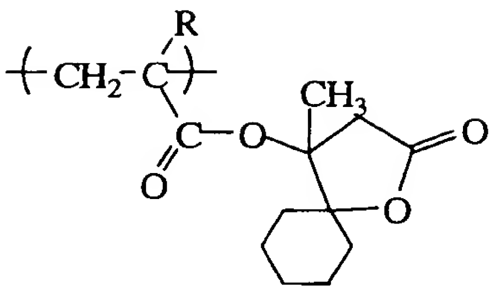

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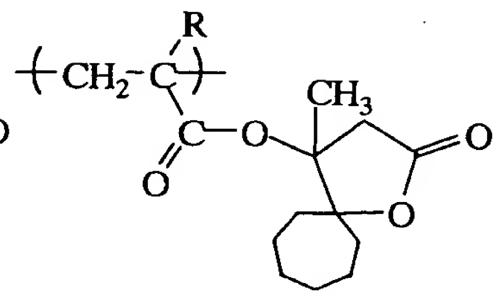


(I-52)

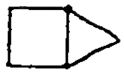
In the present invention, the resin (B) preferably contains a repeating unit having an alkali-soluble group protected by at least one group containing an alicyclic hydrocarbon structure represented by formula (pI), (pII), (pIII), (pIV), (pV) or (pVI), because the effect of the present invention can be more outstandingly brought out.

In formulae (pI) to (pVI), the alkyl group represented by R_{12} to R_{25} represents a linear or branched alkyl group having from 1 to 4 carbon atoms, which may be either substituted or unsubstituted. Examples of the alkyl group include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group and a tert-butyl group.

Examples of the substituent of the alkyl group include an alkoxy group having from 1 to 4 carbon atoms, a halogen atom (e.g., fluorine, chlorine, bromine, iodine), an acyl group, an acyloxy group, a cyano group, a hydroxy group, a carboxy group, an alkoxycarbonyl group and a nitro group.

The alicyclic hydrocarbon group represented by R_{11} to R_{25} and the alicyclic hydrocarbon group formed by Z and the carbon atom may be either monocyclic or polycyclic. Specific examples thereof include a group having 5 to more carbon atoms having a monocyclo-, bicyclo-, tricyclo, tetracyclo-structure. The carbon atom number is preferably from 6 to 30, more preferably from 7 to 25. These alicyclic hydrocarbon group each may have a substituent.

Examples of the structure in the alicyclic moiety of the group containing an alicyclic hydrocarbon structure are shown below.



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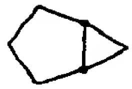

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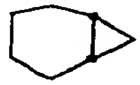

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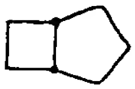

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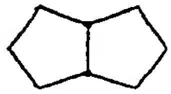

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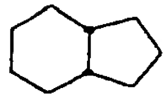

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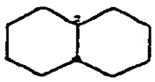

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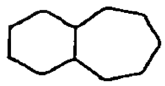

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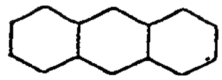

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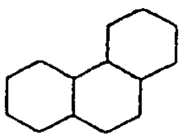

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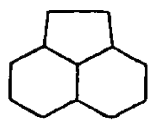

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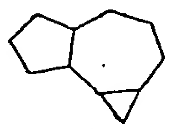

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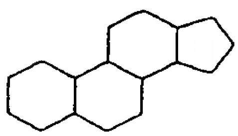

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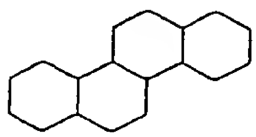

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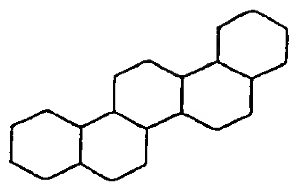

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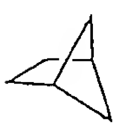

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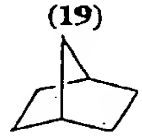

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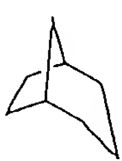

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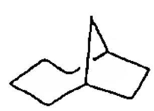

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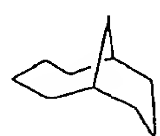

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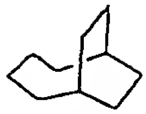
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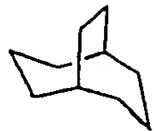
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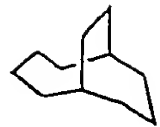
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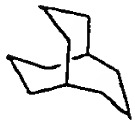
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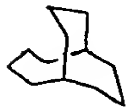
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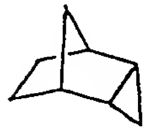
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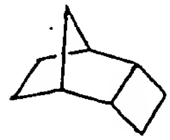
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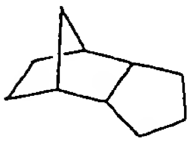
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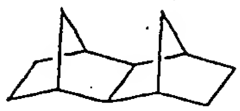
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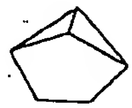
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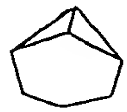
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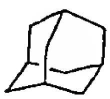
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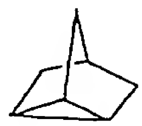
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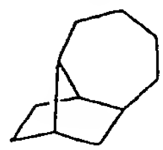
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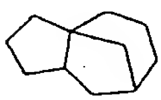
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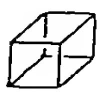
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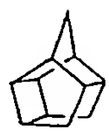
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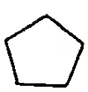
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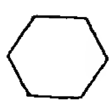
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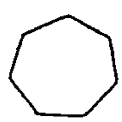
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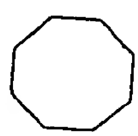
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Among these alicyclic moieties, preferred in the present invention are an adamantyl group, a noradamantyl group, a decaline residue, a tricyclodecanyl group, a tetracyclododecanyl group, a norbornyl group, a cedrol group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclodecanyl group and a cyclododecanyl group, more preferred are an adamantyl group, a decaline residue, a norbornyl group, a cedrol group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclodecanyl group and a cyclododecanyl group.

Examples of the substituent of the alicyclic hydrocarbon group include an alkyl group, a substituted alkyl group, a cycloalkyl group, an alkenyl group an acyl group, a halogen atom, a hydroxyl group, an alkoxy group, a carboxy group and an alkoxycarbonyl group. The alkyl group is preferably a lower alkyl group such as methyl group, ethyl group, propyl group, isopropyl group and butyl group, more preferably a methyl group, an ethyl group, a propyl group or an isopropyl group. Examples of the substituent of the substituted alkyl group include a hydroxyl group, a halogen atom and an alkoxy group.

Examples of the alkoxy group (inclusive of the alkoxy group of the alkoxycarbonyl group) include an alkoxy group having from 1 to 4 carbon atoms, such as methoxy group,

ethoxy group, propoxy group and butoxy group.

Examples of the cycloalkyl group include a cyclopropyl group, a cyclopentyl group and a cyclohexyl group.

Examples of the alkenyl group include an alkenyl group having from 2 to 6 carbon atoms and specific examples thereof include a vinyl group, a propenyl group, an allyl group, a butenyl group, a pentenyl group and a hexenyl group.

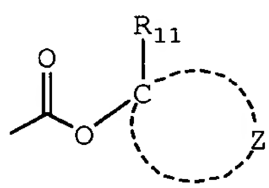
Examples of the acyl group include an acetyl group, an ethylcarbonyl group and a propylcarbonyl group. Examples of the halogen atom include chlorine atom, bromine atom, iodine atom and fluorine atom.

Among the structures represented by formulae (pI) to (pVI), preferred is formula (pI), more preferred is a group represented by formula (II). Examples of the alkyl group represented by R_{28} in formula (II) and examples of the halogen atom, alkyl group, cycloalkyl group, alkenyl group, alkoxy group, alkoxycarbonyl group and acyl group represented by any one of R_{29} to R_{31} include those described above as examples of the substituent of the alicyclic hydrocarbon group.

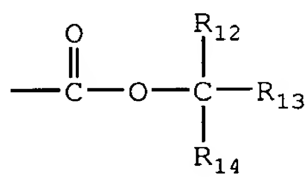
Examples of the alkali-soluble group protected by a structure represented by formula (pI), (pII), (pIII), (pIV), (pV) or (pVI) in the resin include various groups known in

this technical field. Specific examples thereof include a carboxylic acid group, a sulfonic acid group, a phenol group and a thiol group. Among these, preferred are a carboxylic acid group and a sulfonic acid group.

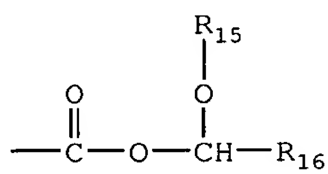
Preferred examples of the alkali-soluble group protected by a structure represented by formula (pI), (pII), (pIII), (pIV), (pV) or (pVI) in the resin include the groups represented by the following formulae (pVII) to (pXI):



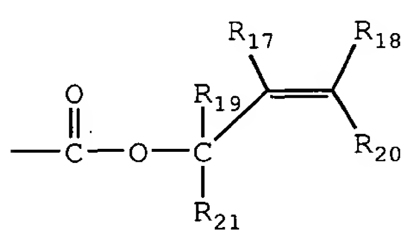
(pVII)



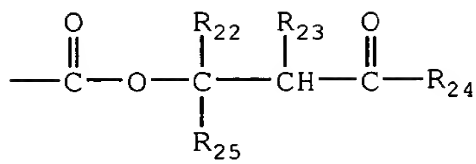
(pVIII)



(pIX)



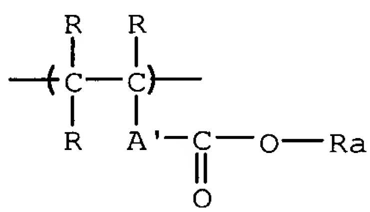
(pX)



(pXI)

wherein R_{11} to R_{25} and Z have the same meanings as defined above.

The repeating unit having an alkali-soluble group protected by a structure represented by formula (pI), (pII), (pIII), (pIV), (pV) or (pVI), constituting the resin is preferably a repeating unit represented by the following formula (pA):



(pA)

In formula (pA), R represents hydrogen atom, a halogen atom or a substituted or unsubstituted, linear or branched alkyl group having from 1 to 4 carbon atoms, the plurality of R groups may be the same or different, and examples of the halogen atom and the alkyl group represented by R are the same as the examples of R in formula (a).

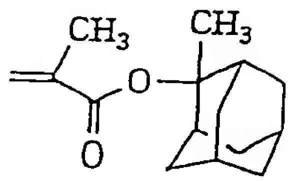
A' has the same meaning as defined above.

Ra represents any one group of (pI), (pII), (pIII), (pIV), (pV) and (pVI).

Specific examples of the monomer corresponding to the

repeating unit represented by formula (pA) are set forth below.

1



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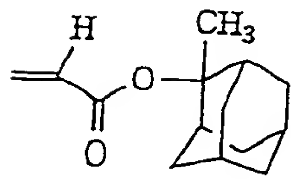

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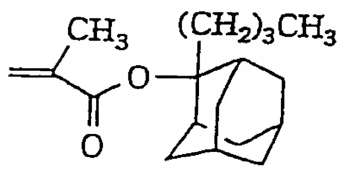

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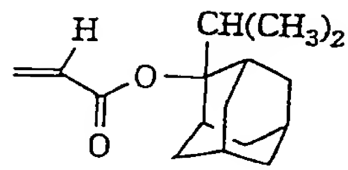

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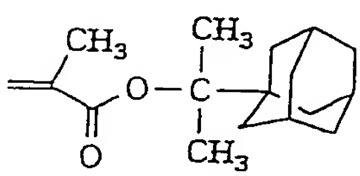

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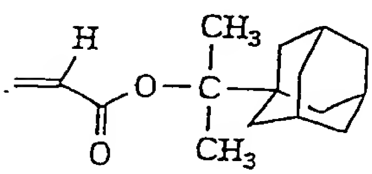

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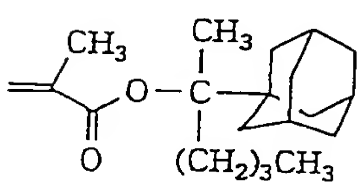

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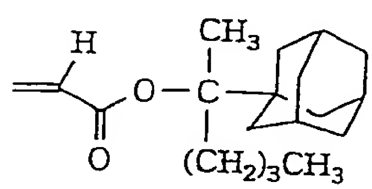

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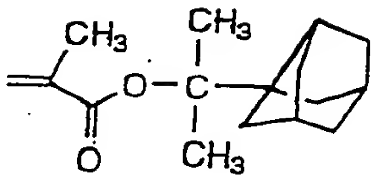

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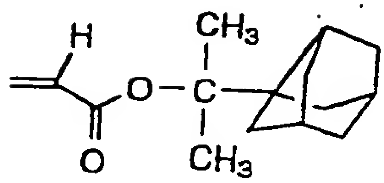

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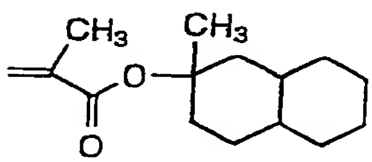

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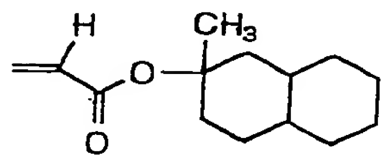

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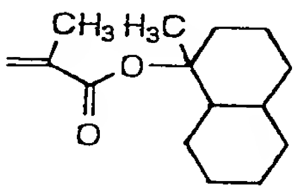

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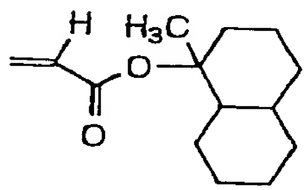

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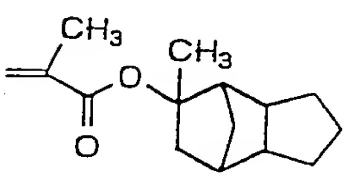

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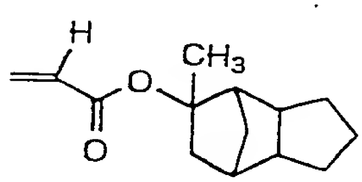

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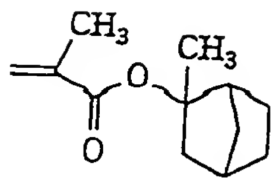

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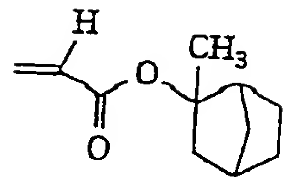

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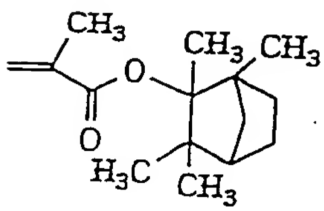

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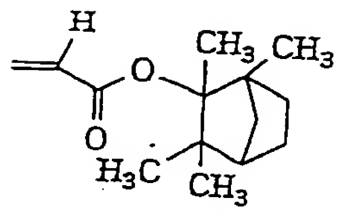

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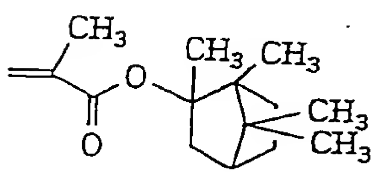

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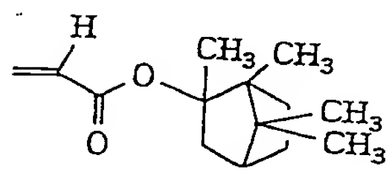

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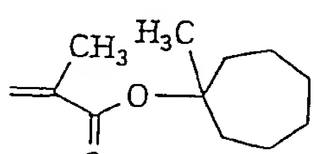

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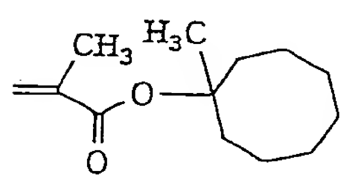

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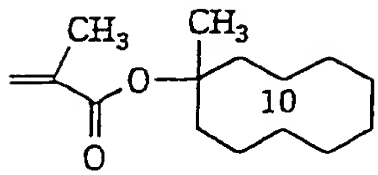

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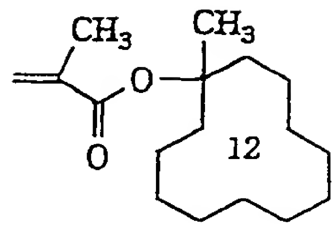

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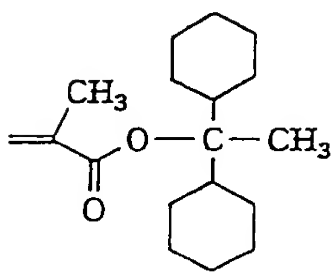

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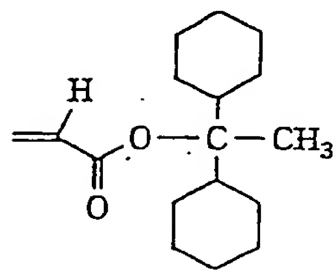

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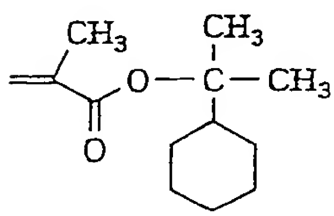

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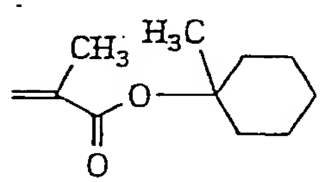

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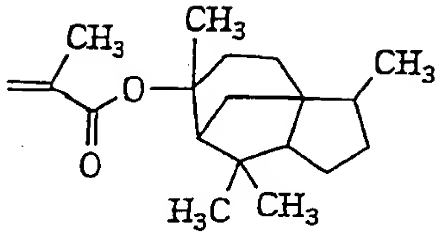

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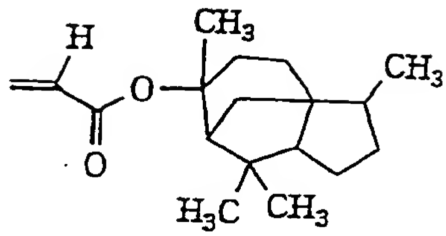

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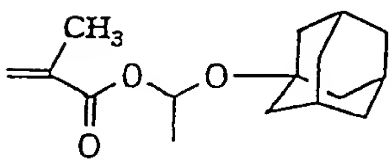

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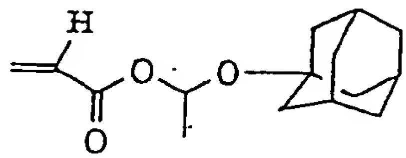

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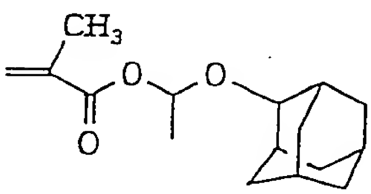

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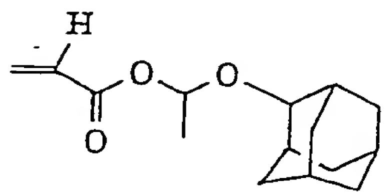

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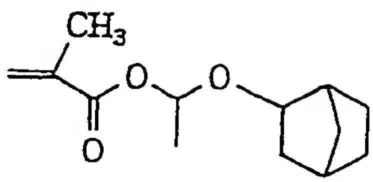

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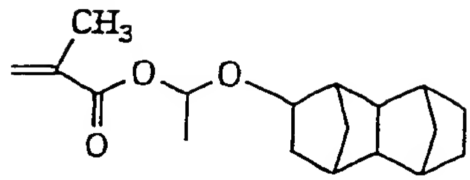

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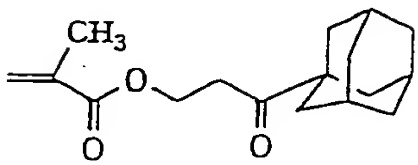

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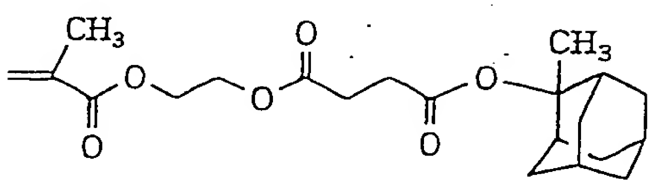

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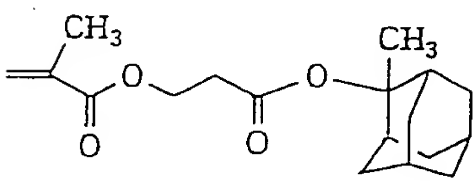
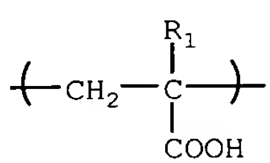


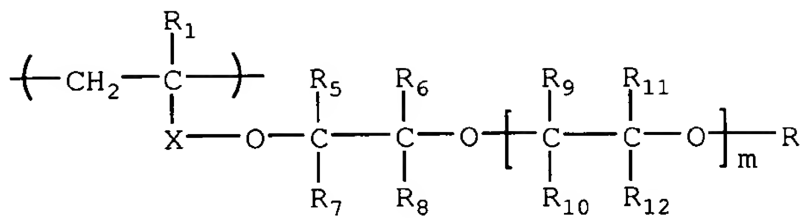
The resin (B) may further contain another repeating unit.

The resin (B) for use in the present invention preferably contains, as another copolymerization component, the repeating unit represented by formula (a), because the developability or the adhesive property to a substrate is improved. Examples of the alkyl group which may have a substituent, represented by R in formula (a), are the same as the examples of R_1 in formula (I). Examples of the halogen atom represented by R include fluorine atom, chlorine atom, bromine atom and iodine atom. In formula (a), at least one of R_{32} to R_{34} is a hydroxyl group, preferably a dihydroxy form or a monohydroxy form, more preferably a monohydroxy form.

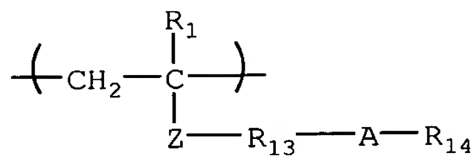
The resin (B) for use in the present invention preferably further contains, as another copolymerization component, a repeating unit represented by the following formula (III-a), (III-b), (III-c) or (III-d), because the releasability of the exposure part between patterns at the development is improved and the resolution of the contact whole pattern is improved.



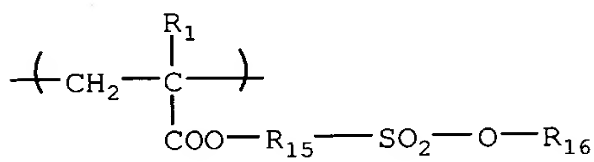
(III-a)



(III-b)



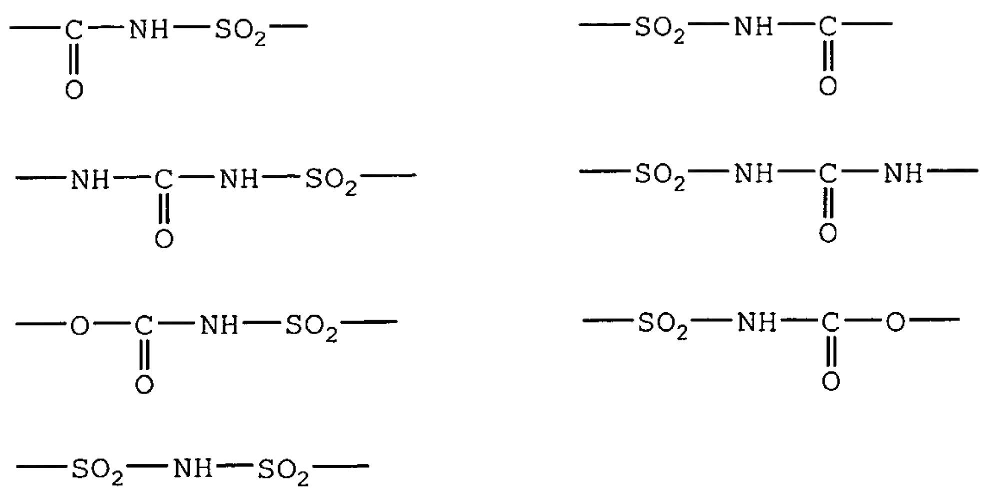
(III-c)



(III-d)

wherein R_1 has the same meaning as R defined above, R_5 to R_{12} each independently represents hydrogen atom or an alkyl group which may have a substituent, R represents hydrogen atom, an alkyl group which may have a substituent, a cyclic alkyl group which may have a substituent, an aryl group which may have a substituent or an aralkyl group which may have a substituent, m represents an integer of 1 to 10, X represents a single bond, an alkylene group which may have a substituent, a cyclic alkylene group which may have a substituent, an arylene group which may have a substituent, or a divalent group which comprises one group or a combination of two or more groups selected from the group consisting of an ether group, a thioether group, a carbonyl group, an ester group, an amido group, a sulfonamido group,

a urethane group and a urea group and which does not decompose under the action of an acid, Z represents a single bond, an ether group, an ester group, an amido group, an alkylene group or a divalent group comprising a combination thereof, R_{13} represents a single bond, an alkylene group, an arylene group or a divalent group comprising a combination thereof, R_{15} represents an alkylene group, an arylene group or a divalent group comprising a combination thereof, R_{14} represents an alkyl group which may have a substituent, a cyclic alkyl group which may have a substituent, an aryl group which may have a substituent or an aralkyl group which may have a substituent, R_{16} represents hydrogen atom, an alkyl group which may have a substituent, a cyclic alkyl group which may have a substituent, an alkenyl group which may have a substituent, an aryl group which may have a substituent or an aralkyl group which may have a substituent, and A represents any one of the functional groups shown below:



Examples of the alkyl group represented by any one of R_5 to R_{12}, R, R_{14} and R_{16} include a linear or branched alkyl group which may have a substituent. The linear or branched alkyl group is preferably a linear or branched alkyl group having from 1 to 12 carbon atoms, more preferably a linear or branched alkyl group having from 1 to 10 carbon atoms, still more preferably a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group or a decyl group.

Examples of the cyclic alkyl group represented by R, R_{14} or R_{16} include a cyclic alkyl group having from 3 to 30 carbon atoms and specific examples thereof include a cyclopropyl group, a cyclopentyl group, a cyclohexyl group,

an adamantyl group, a norbornyl group, a boronyl group, a tricyclodecanyl group, a dicyclopentenyl group, a norbornane epoxy group, a menthyl group, an isomenthyl group, a neomenthyl group, a tetracyclododecanyl group and a steroid residue.

Examples of the aryl group represented by R, R_{14} or R_{16} include an aryl group having from 6 to 20 carbon atoms, which may have a substituent. Specific examples thereof include a phenyl group, a tolyl group and a naphthyl group.

Examples of the aralkyl group represented by R, R_{14} or R_{16} include an aralkyl group having from 7 to 20 carbon atoms, which may have a substituent. Specific examples thereof include a benzyl group, a phenethyl group and a cumyl group.

Examples of the alkenyl group represented by R_{16} include an alkenyl group having from 2 to 6 carbon atoms. Specific examples thereof include a vinyl group, a propenyl group, an allyl group, a butenyl group, a pentenyl group, a hexenyl group, a cyclopentenyl group, a cyclohexenyl group, a 3-oxocyclohexenyl group, a 3-oxocyclopentenyl group and a 3-oxoindenyl group. Among these, the cyclic alkenyl groups each may contain oxygen atom.

Examples of the linking group X include an alkylene group which may have a substituent, a cyclic alkylene group

which may have a substituent, an arylene group which may have a substituent, or a divalent group which comprises one group or a combination of two or more groups selected from the group consisting of an ether group, a thioether group, a carbonyl group, an ester group, an amido group, a sulfonamido group, a urethane group and a urea group and which does not decompose under the action of an acid.

Z represents a single bond, an ether group, an ester group, an amido group, an alkylene group or a divalent group comprising a combination thereof. R_{13} represents a single bond, an alkylene group, an arylene group or a divalent group comprising a combination thereof. R_{15} represents an alkylene group, an arylene group or a divalent group comprising a combination thereof.

Examples of the arylene group represented by X, R_{13} or R_{15} include an arylene group having from 6 to 10 carbon atoms, which may have a substituent. Specific examples thereof include a phenylene group, a tolylene group and a naphthylene group.

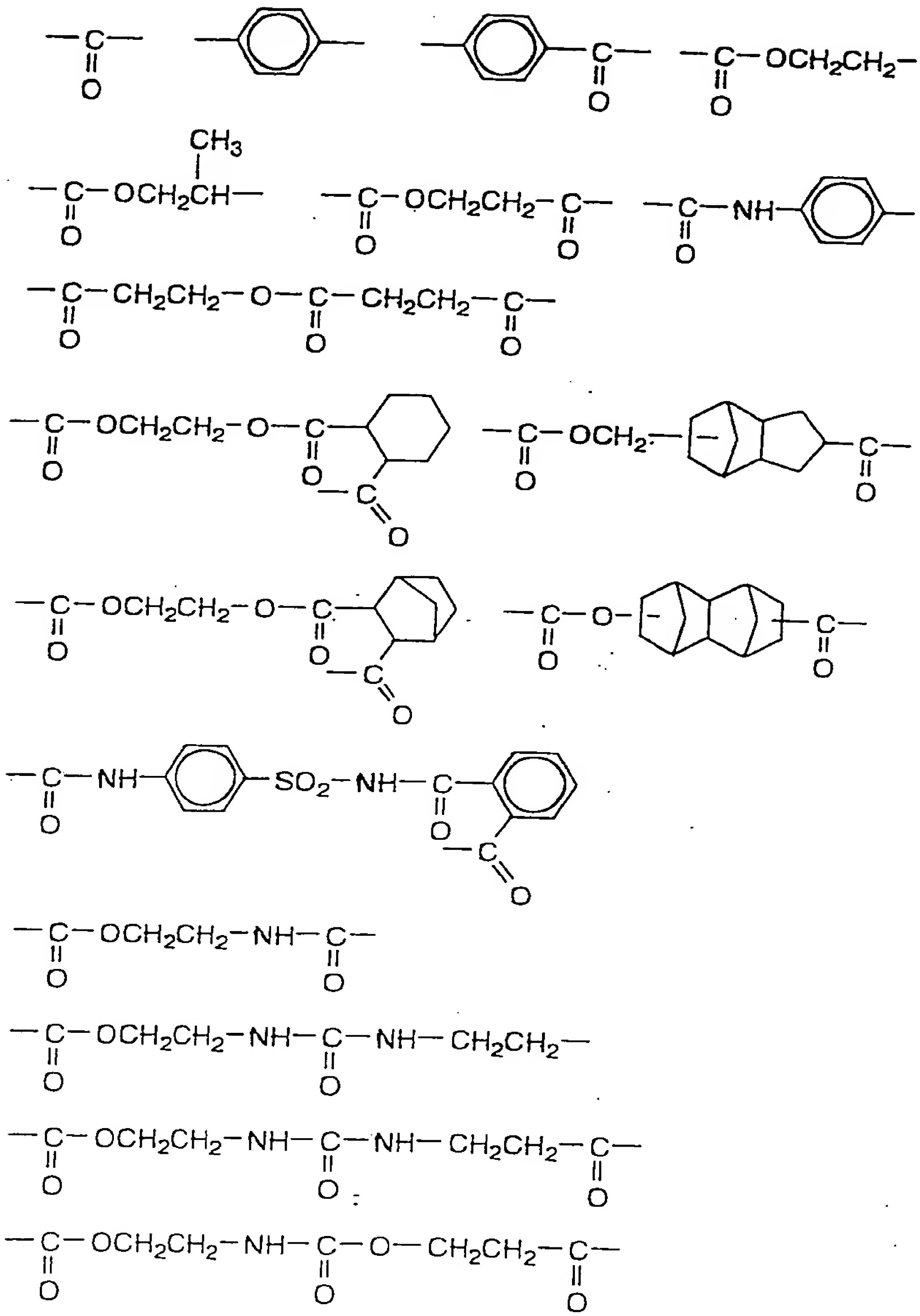
Examples of the cyclic alkylene group represented by X include divalent groups formed from the above-described cyclic alkyl groups.

Examples of the alkylene group represented by X, Z, R_{13} or R_{15} include a group represented by the following formula:

$$-[C(Ra)(Rb)]_{r1}-$$

wherein Ra and Rb, which may be the same or different, each represents hydrogen atom, an alkyl group, a substituted alkyl group, a halogen atom, a hydroxyl group or an alkoxy group. The alkyl group is preferably a lower alkyl group such as methyl group, ethyl group, propyl group, isopropyl group and butyl group, more preferably a methyl group, an ethyl group, a propyl group or an isopropyl group. Examples of the substituent of the substituted alkyl group include a hydroxyl group, a halogen atom and an alkoxy group. Examples of the alkoxy group include an alkoxy group having from 1 to 4 carbon atoms, such as methoxy group, ethoxy group, propoxy group and butoxy group. Examples of the halogen atom include chlorine atom, bromine atom, fluorine atom and iodine atom. r1 represents an integer of 1 to 10.

Specific examples of the linking group X are set forth below, however, the present invention is by no means limited thereto.



Examples of the substituent in the above-described alkyl group, cyclic alkyl group, alkenyl group, aryl group, aralkyl group, alkylene group, cyclic alkylene group and arylene group include a carboxyl group, an acyloxy group, a cyano group, an alkyl group, a substituted alkyl group, a halogen atom, a hydroxyl group, an alkoxy group, an acetylamido group, an alkoxycarbonyl group and an acyl group. Examples of the alkyl group include a lower alkyl group such as methyl group, ethyl group, propyl group, isopropyl group, butyl group, cyclopropyl group, cyclobutyl group and cyclopentyl group. Examples of the substituent of the substituted alkyl group include a hydroxyl group, a halogen atom and an alkoxy group. Examples of the alkoxy group include an alkoxy group having from 1 to 4 carbon atoms, such as methoxy group, ethoxy group, propoxy group and butoxy group. Examples of the acyloxy group include an acetoxy group. Examples of the halogen atom include chlorine atom, bromine atom, fluorine atom and iodine atom.

Specific examples of the structure of the side chain in formula (III-b) are set forth below, where specific examples of the structure of the terminal moiety exclusive of X are shown, however, the present invention is by no means limited thereto.

$$-O-CH_2CH_2-O-CH_2CH_2-OH$$

$$-O-CH_2CH_2-O-CH_2CH_2-O-CH_3$$

$$-O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_3$$

$$-O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-OH$$

$$-O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-O-CH_3$$

$$-O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_3$$

$$-O-CH_2\underset{\substack{|\\ CH_3}}{C}H-O-CH_2\underset{\substack{|\\ CH_3}}{C}H-O-CH_3$$

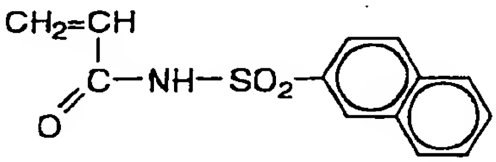
$$-O-\underset{\substack{|\\ CH_3}}{C}HCH_2-O-\underset{\substack{|\\ CH_3}}{C}HCH_2-O-CH_3$$

$$-O-CH_2\underset{\substack{|\\ CH_3}}{C}H-O-CH_2\underset{\substack{|\\ CH_3}}{C}H-O-CH_2\underset{\substack{|\\ CH_3}}{C}H-O-CH_3$$

$$-O-CH_2CH_2-\left(O-CH_2CH_2\right)_3-O-CH_3$$

$$-O-CH_2CH_2-\left(O-CH_2CH_2\right)_4-O-CH_3$$

Specific examples of the monomer corresponding to the repeating structural unit represented by formula (III-c) are set forth below, however, the present invention is by no means limited thereto.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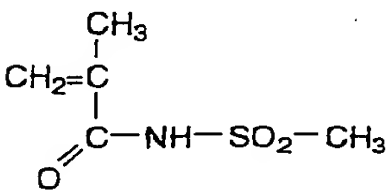
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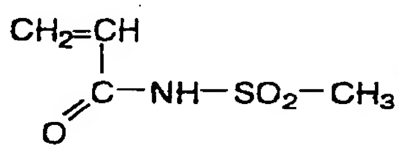
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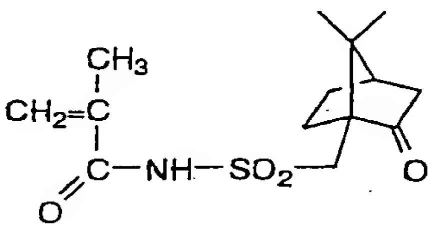
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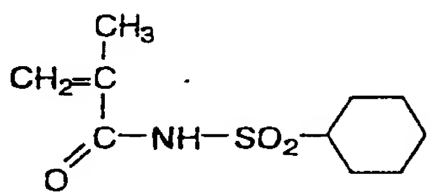
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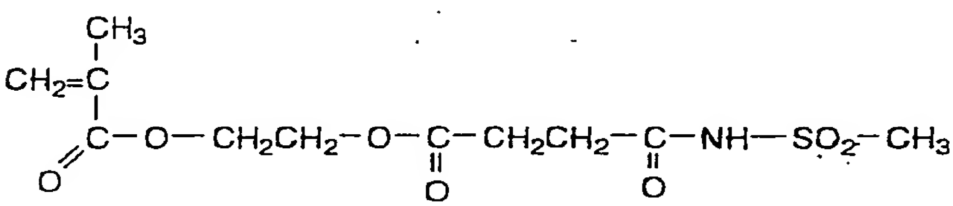
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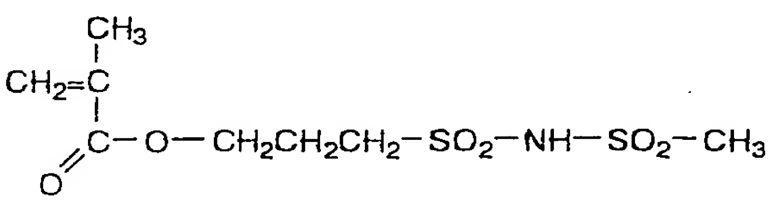
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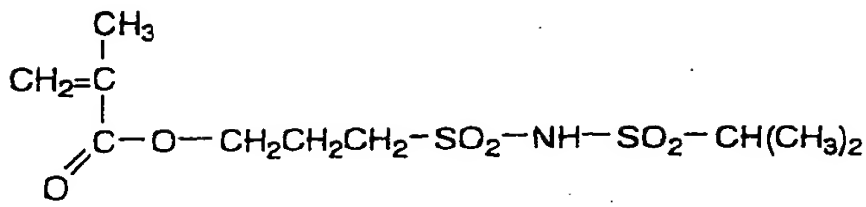

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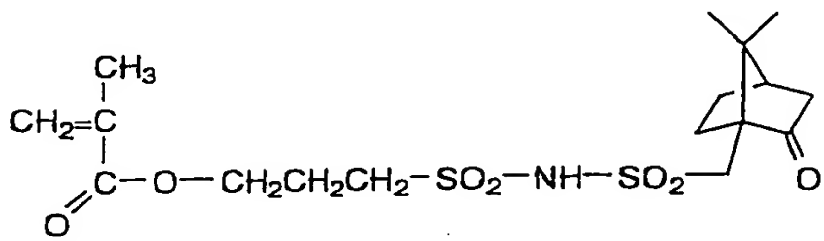

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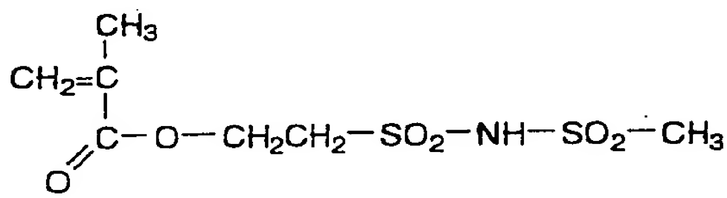

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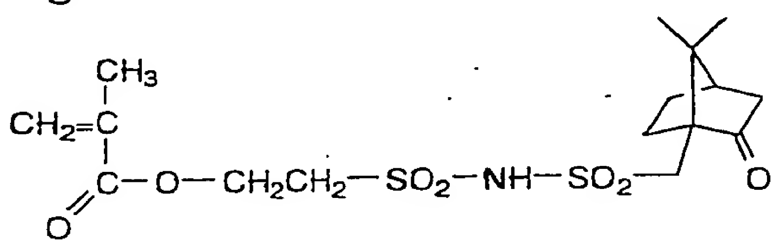

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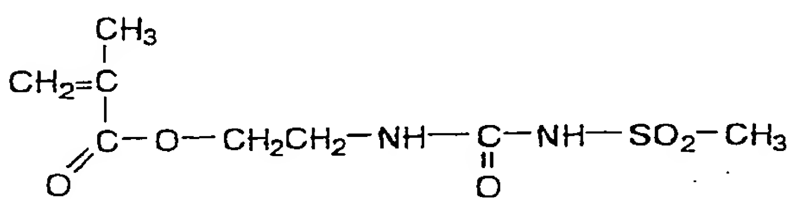

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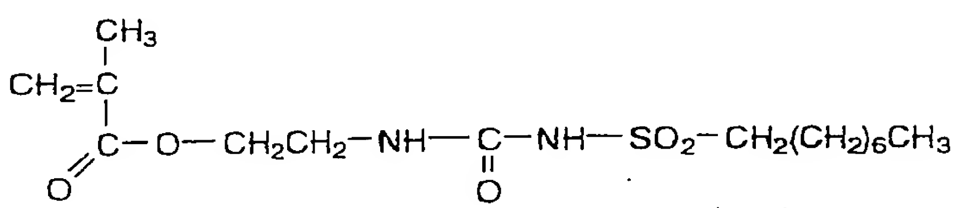

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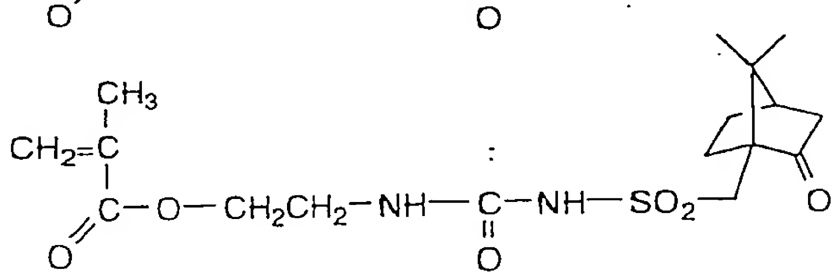

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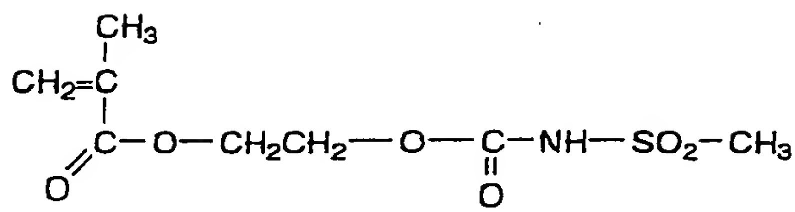

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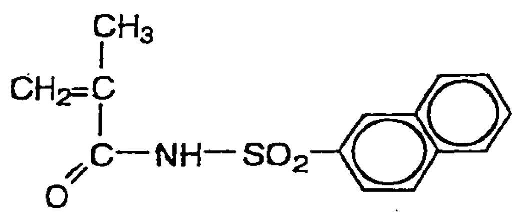

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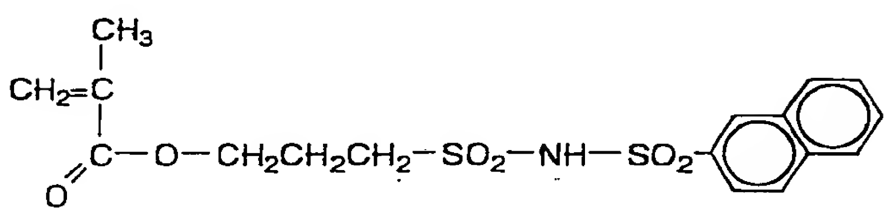
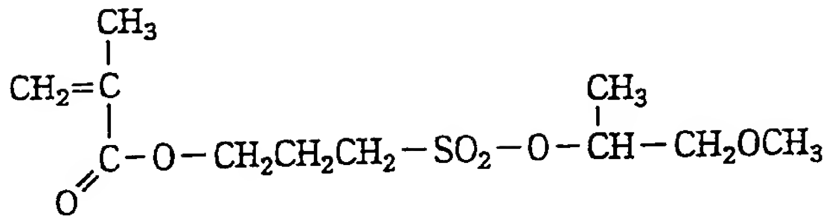


(17)

Specific examples of the repeating structural unit represented by formula (III-d) are set forth below, however, the present invention is by no means limited thereto.



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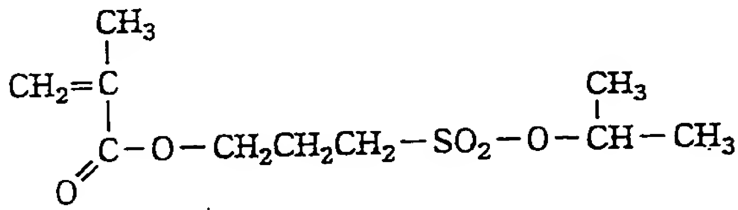

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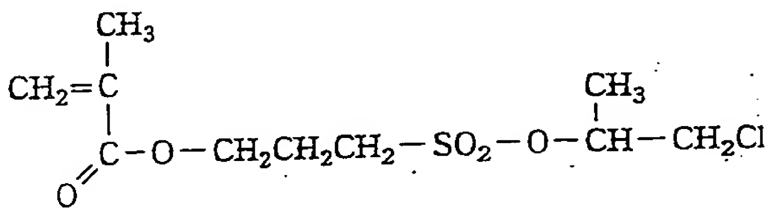

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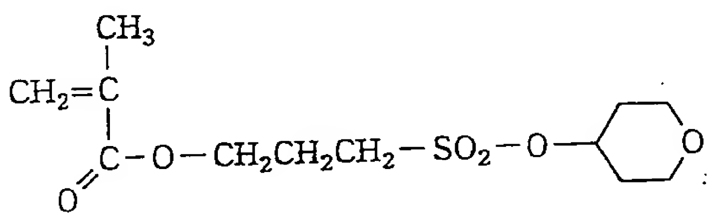

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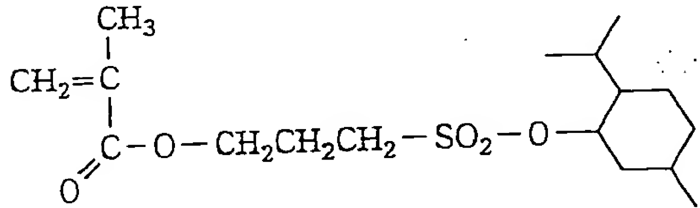

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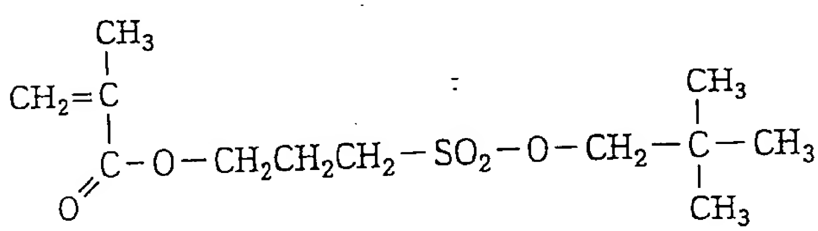

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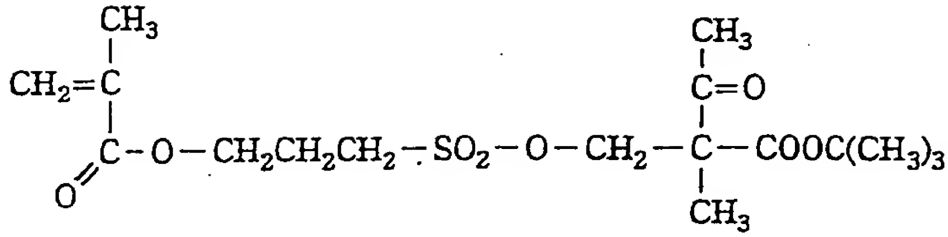

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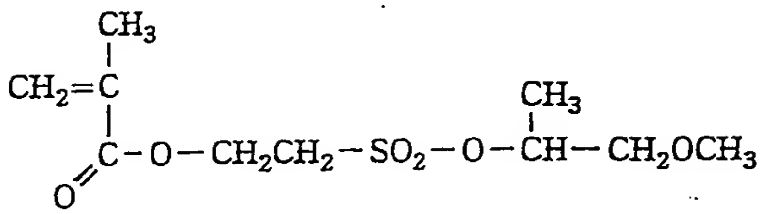

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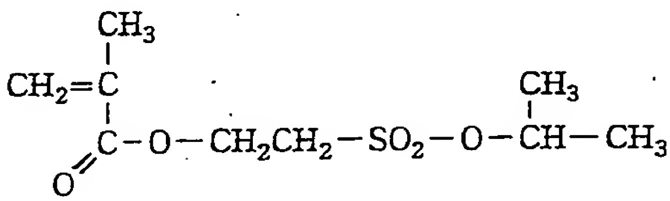

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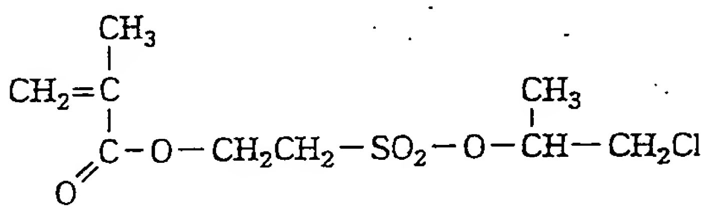

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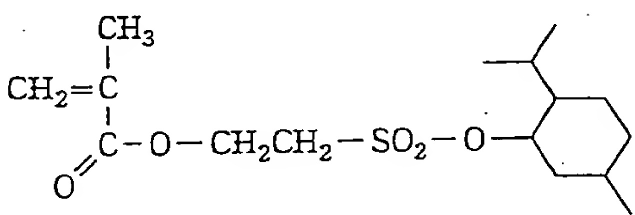

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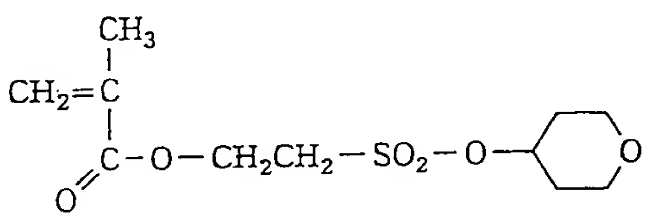

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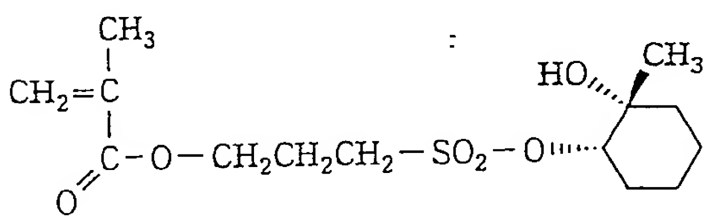

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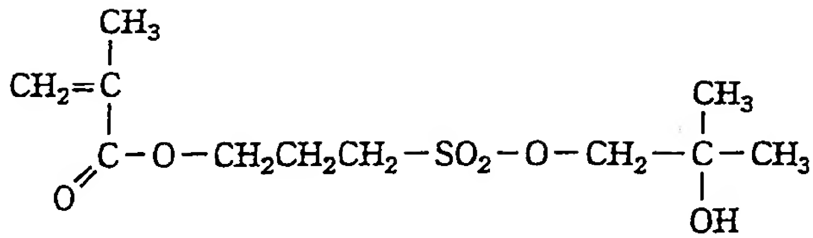

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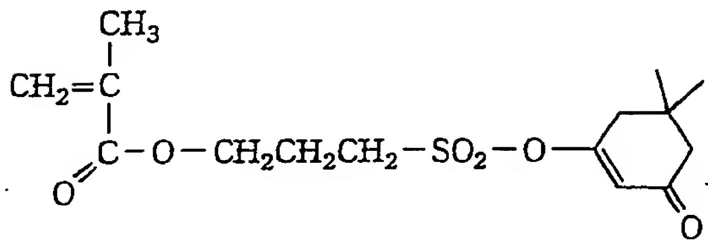

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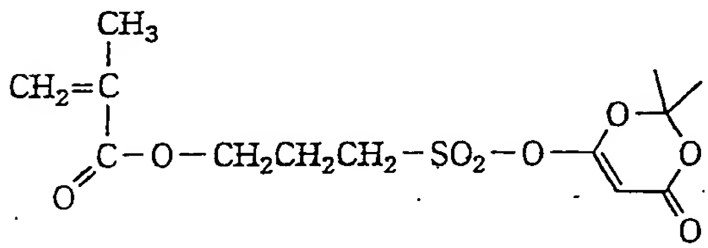

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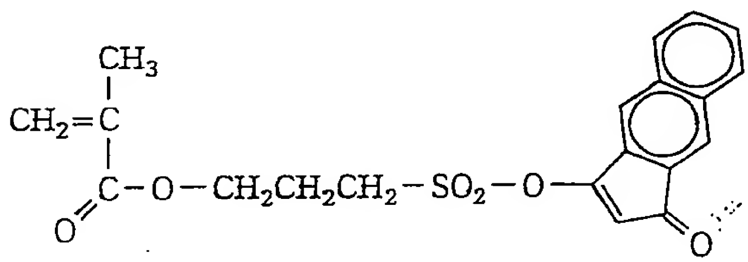

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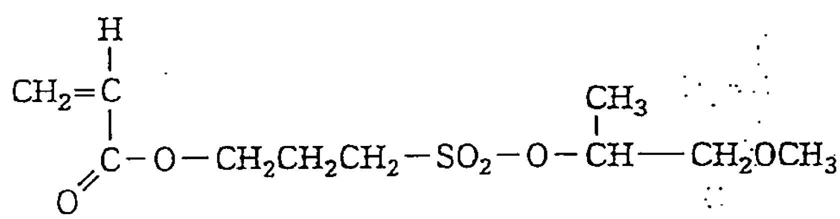

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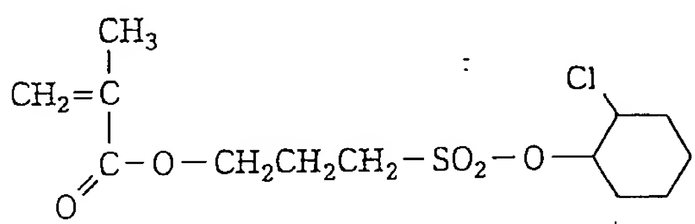


(19)

In formula (III-b), R_5 to R_{12} each is preferably hydrogen atom or a methyl group. R is preferably hydrogen atom or an alkyl group having from 1 to 4 carbon atoms. m is preferably a number of 1 to 6.

In formula (III-c), R_{13} is preferably a single bond or an alkylene group such as methylene group, ethylene group, propylene group and butylene group. R_{14} is preferably an alkyl group having from 1 to 10 carbon atoms, such as methyl group and ethyl group, a cyclic alkyl group such as cyclopropyl group, cyclohexyl group and camphor residue, a naphthyl group or a naphthylmethyl group. Z is preferably a single bond, an ether bond, an ester bond, an alkylene group having from 1 to 6 carbon atoms or a combination thereof, more preferably a single bond or an ester bond.

In formula (III-d), R_{15} is preferably an alkylene group having from 1 to 4 carbon atoms. R_{16} is preferably an alkyl group having from 1 to 8 carbon atoms, such as methyl group which may have a substituent, ethyl group which may have a substituent, propyl group which may have a substituent, isopropyl group which may have a substituent, butyl group which may have a substituent, neopentyl group which may have a substituent and octyl group which may have a substituent, a cyclohexyl group, an adamantyl group, a norbornyl group, a boronyl group, an isoboronyl group, a

menthyl group, a morpholino group, a 4-oxocyclohexyl group, a phenyl group which may have a substituent, a toluyl group which may have a substituent, a mesityl group which may have a substituent, a naphthyl group which may have a substituent or a camphor residue which may have a substituent. The substituent of these groups is preferably a halogen atom such as fluorine atom, or an alkoxy group having from 1 to 4 carbon atoms.

In the present invention, among the repeating units represented by formulae (III-a) to (III-d), those represented by formulae (III-b) and (III-d) are preferred.

The resin (B) may be used, in addition to the above-described use, as a copolymer with a monomer repeating unit of various types for the purpose of controlling the dry etching resistance, the suitability for standard developer, the adhesion to a substrate, the resist profile and the general factors required for the resist, such as resolution, heat resistance and sensitivity.

Examples of such a repeating unit include the repeating units corresponding to the following monomers, however, the present invention is by no means limited thereto.

By virtue of this repeating unit, the capabilities required for the resin, particularly (1) solubility in the

coating solvent, (2) film-forming property (glass transition point), (3) alkali developability, (4) film thickness loss (selection of hydrophilic/hydrophobic or alkali-soluble group), (5) adhesion to a substrate in the unexposed area and (6) dry etching resistance, can be subtly controlled.

Examples of this copolymerization monomer include compounds having one addition-polymerizable unsaturated bond selected from acrylic acid esters, methacrylic acid esters, acrylamides, methacrylamides, allyl compounds, vinyl ethers and vinyl esters.

Specific examples thereof include acrylic acid esters such as alkyl (the alkyl group preferably has from 1 to 10 carbon atoms) acrylates (e.g., methyl acrylate, ethyl acrylate, propyl acrylate, amyl acrylate, cyclohexyl acrylate, ethylhexyl acrylate, octyl acrylate, tert-octyl acrylate, chloroethyl acrylate, 2-hydroxyethyl acrylate, 2,2-dimethylhydroxypropyl acrylate, 5-hydroxypentyl acrylate, trimethylolpropane monoacrylate, pentaerythritol monoacrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate);

methacrylic acid esters such as alkyl (the alkyl group preferably has from 1 to 10 carbon atoms) methacrylates (e.g., methyl methacrylate, ethyl methacrylate, propyl

methacrylate, isopropyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, chlorobenzyl methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxybutyl methacrylate, 5-hydroxypentyl methacrylate, 2,2-dimethyl-3-hydroxypropyl methacrylate, trimethylolpropane monomethacrylate, pentaerythritol monomethacrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate);

acrylamides such as acrylamide, N-alkylacrylamides (where the alkyl group has from 1 to 10 carbon atoms, such as methyl group, ethyl group, propyl group, butyl group, tert-butyl group, heptyl group, octyl group, cyclohexyl group and hydroxyethyl group), N,N-dialkylacrylamides (where the alkyl group has from 1 to 10 carbon atoms, such as methyl group, ethyl group, butyl group, isobutyl group, ethylhexyl group and cyclohexyl group), N-hydroxyethyl-N-methylacrylamide and N-2-acetamidoethyl-N-acetylacrylamide;

methacrylamides such as methacrylamide, N-alkyl-methacrylamides (where the alkyl group has from 1 to 10 carbon atoms, such as methyl group, ethyl group, tert-butyl group, ethylhexyl group, hydroxyethyl group and cyclohexyl group), N,N-dialkylmethacrylamides (where the alkyl group is an ethyl group, a propyl group or a butyl group) and N-hydroxyethyl-N-methylmethacrylamide;

allyl compounds such as allyl esters (e.g., allyl acetate, allyl caproate, allyl caprate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate, allyl lactate) and allyloxy ethanol;

vinyl ethers such as alkyl vinyl ethers (e.g., hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, ethylhexyl vinyl ether, methoxyethyl vinyl ether, ethoxyethyl vinyl ether, chloroethyl vinyl ether, 1-methyl-2,2-dimethylpropyl vinyl ether, 2-ethylbutyl vinyl ether, hydroxyethyl vinyl ether, diethylene glycol vinyl ether, dimethylaminoethyl vinyl ether, diethylaminoethyl vinyl ether, butylaminoethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether);

vinyl esters such as vinyl butyrate, vinyl isobutyrate, vinyl trimethylacetate, vinyl diethylacetate, vinyl valerate, vinyl caproate, vinyl chloroacetate, vinyl dichloroacetate, vinyl methoxyacetate, vinyl butoxyacetate, vinyl acetoacetate, vinyl lactate, vinyl-β-phenyl butyrate and vinyl chlorohexylcarboxylate;

dialkyl itaconates (e.g., dimethyl itaconate, diethyl itaconate, dibutyl itaconate); dialkyl esters of fumaric acid (e.g., dibutyl fumarate) and monoalkyl esters of fumaric acid; and

acrylic acid, methacrylic acid, crotonic acid,

itaconic acid, maleic acid anhydride, maleimide, acrylonitrile, methacrylonitrile and maleylonitrile. Other than these, addition-polymerizable unsaturated compounds capable of copolymerizing with the above-described various repeating units may be used.

In the resin (B), the content in molar ratio of each repeating unit may be appropriately selected so as to control the acid value, the dry etching resistance of the resist, the suitability for the standard developer, the adhesion to a substrate, the defocus latitude depended on line pitch of the resist profile, and general properties required for the resist, such as resolution, heat resistance and sensitivity.

The content of the repeating unit represented by formula (I) in the resin (B) is from 30 to 70 mol%, preferably from 35 to 65 mol%, more preferably from 40 to 60 mol%, based on all repeating units.

The content of the repeating unit having a group represented by formula (pI), (pII), (pIII), (pIV), (pV) or (pVI) is usually from 20 to 75 mol%, preferably from 25 to 70 mol%, more preferably from 30 to 65 mol%, based on all repeating units.

The content of the repeating unit represented by formula (a) in the resin (B) is usually from 0 to 70 mol%,

preferably from 10 to 40 mol%, more preferably from 15 to 30 mol%, based on all repeating units.

The content of the repeating unit represented by any one of formulae (IIIa) to (III-d) in the resin (B) is usually from 0.1 to 30 mol%, preferably from 0.5 to 25 mol%, more preferably from 1 to 20 mol%, based on all repeating units.

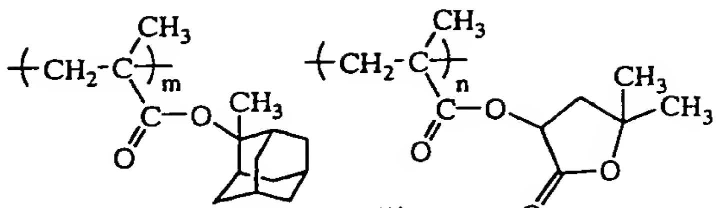
The content of the repeating unit based on the monomer as another copolymerization component in the resin may also be appropriately selected according to the desired resist performance, however, in general, it is preferably 99 mol% or less, more preferably 90 mol% or less, still more preferably 80 mol% or less, based on the total molar number of the repeating unit containing a group represented by formula (I) and the repeating unit having a group represented by formula (pI), (pII), (pIII), (pIV), (pV) or (pVI).

The resin (B) preferably has a weight average molecular weight Mw, measured by a gel permeation chromatography method and calculated in terms of polystyrene, of 1,000 to 1,000,000, more preferably 1,500 to 500,000, still more preferably 2,000 to 200,000, particularly preferably 2,500 to 100,000. As the weight-average molecular weight is larger, the heat resistance

increases but the developability decreases. Therefore, the Mw is controlled to a preferred range by taking account of the balance therebetween.

The resin (B) for use in the present invention can be synthesized according to an ordinary method, for example, by a radical polymerization method.

Specific examples of the resin (B) for use in the present invention are set forth below, however, the present invention is by no means limited thereto.



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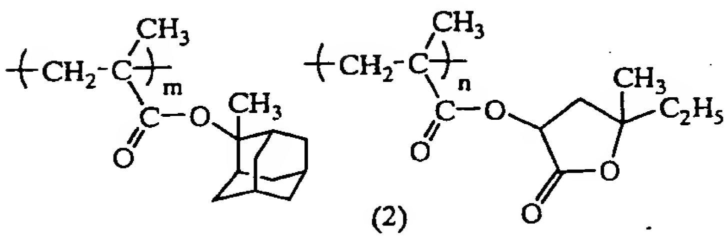

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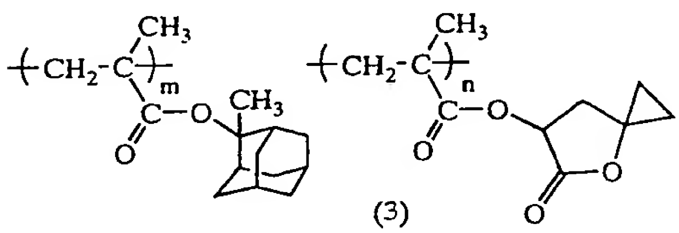

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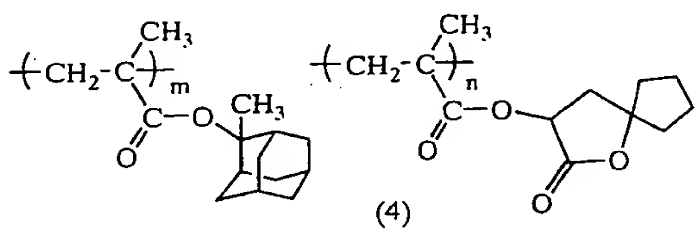

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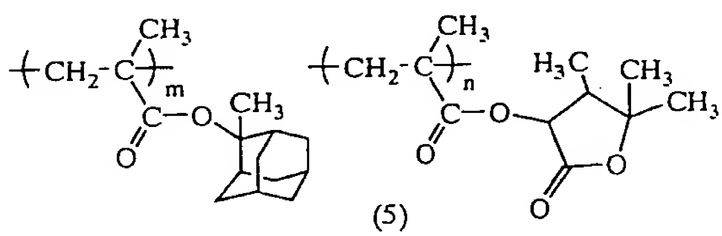

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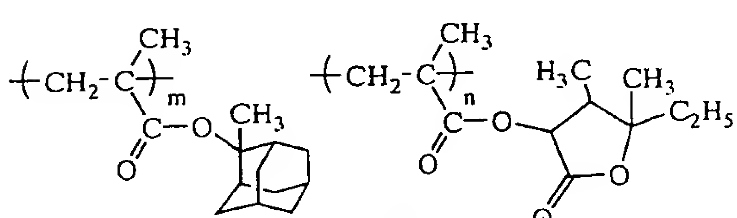

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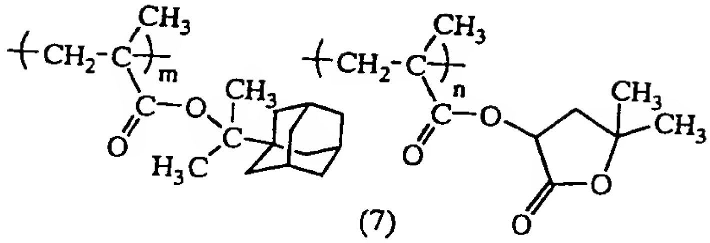

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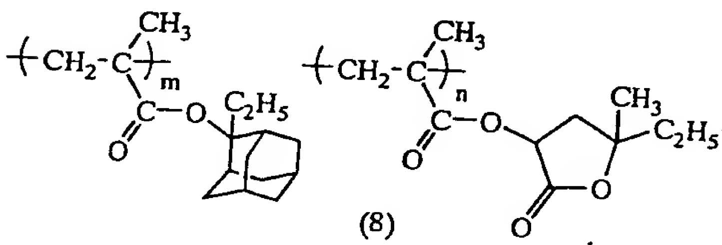

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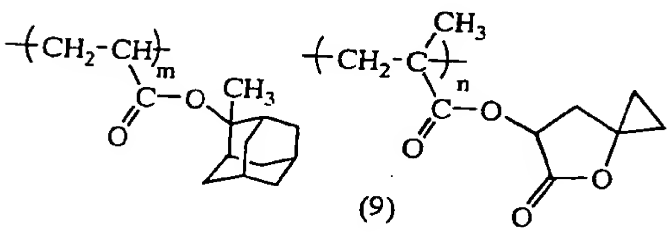

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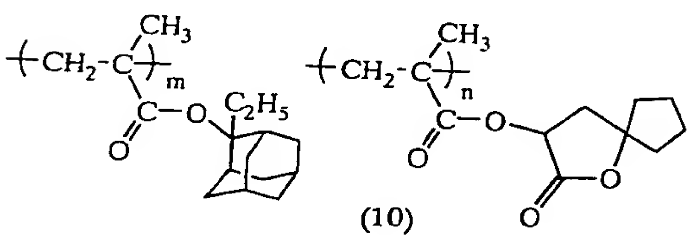

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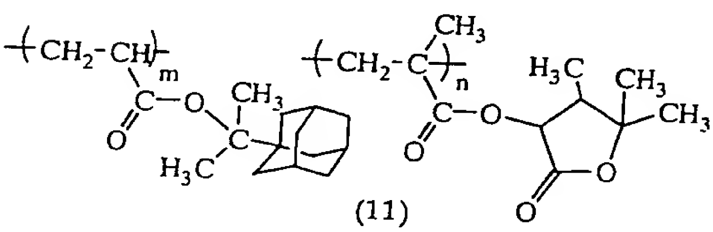

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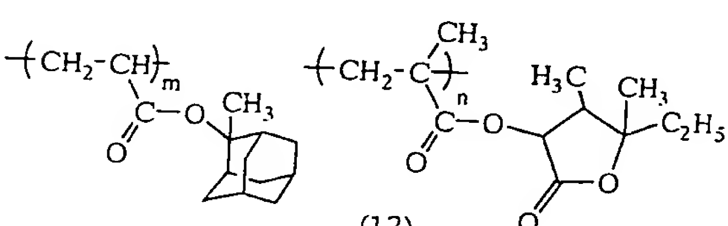

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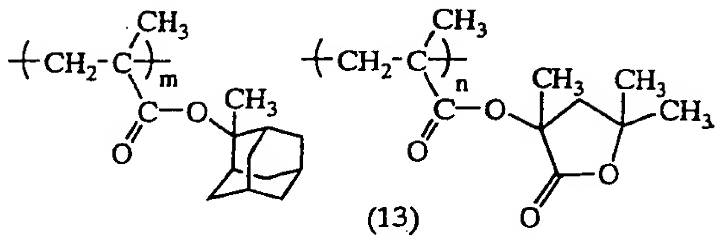

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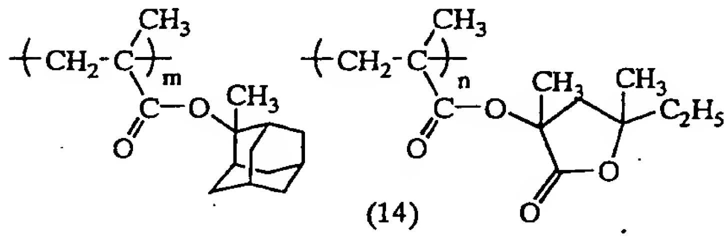

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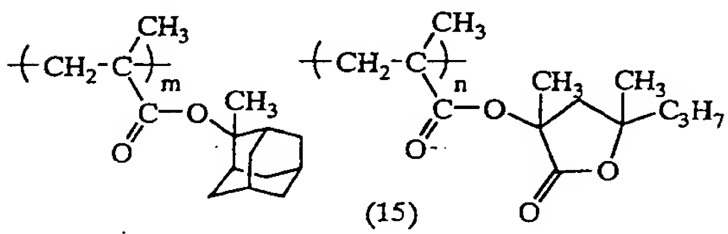

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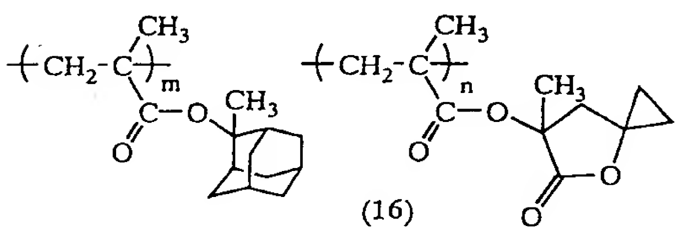

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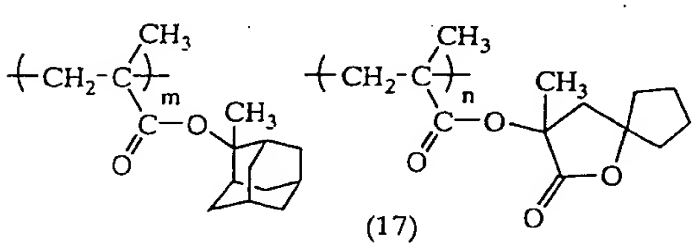

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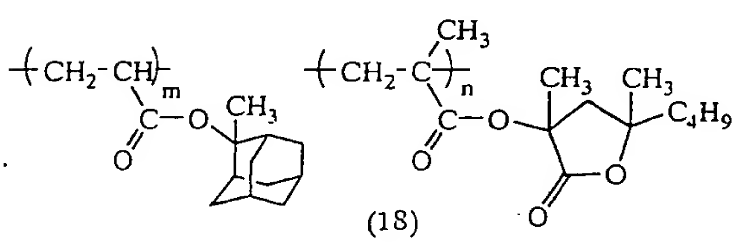

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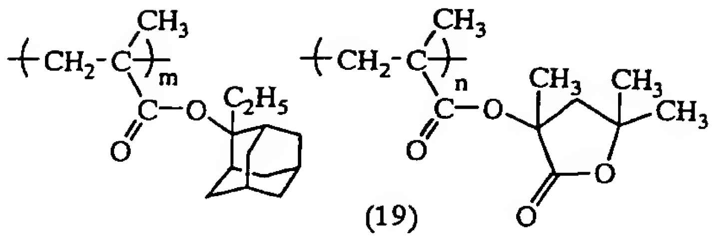

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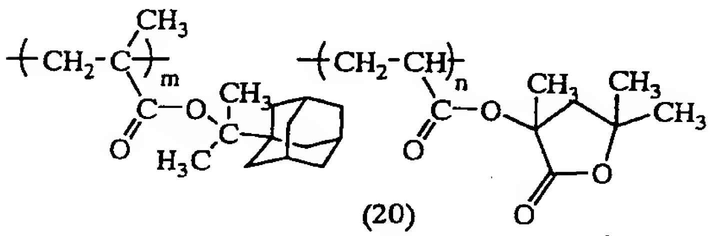

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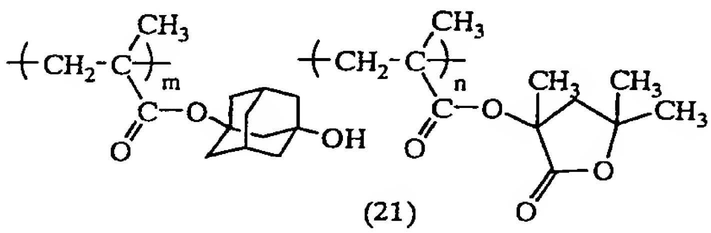

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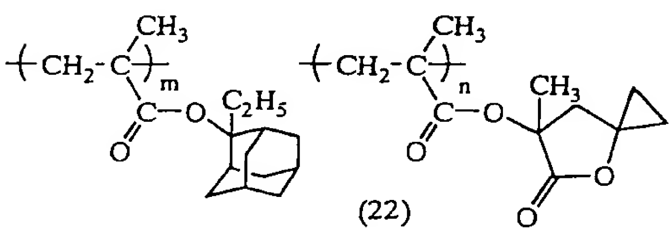

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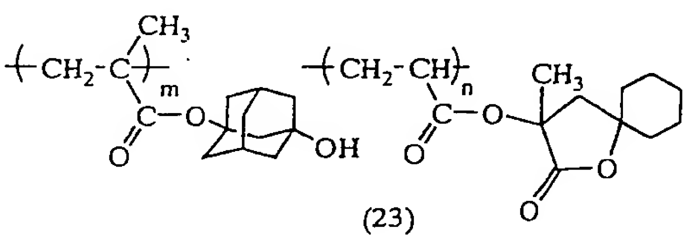

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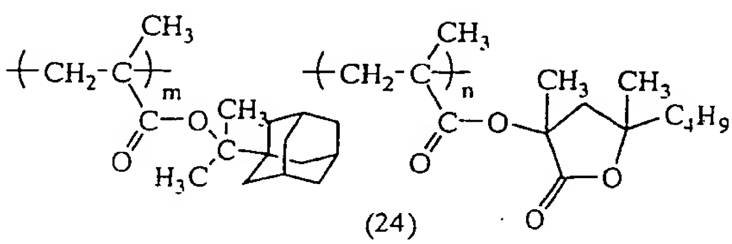

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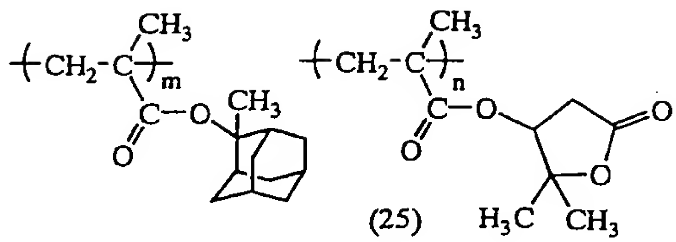

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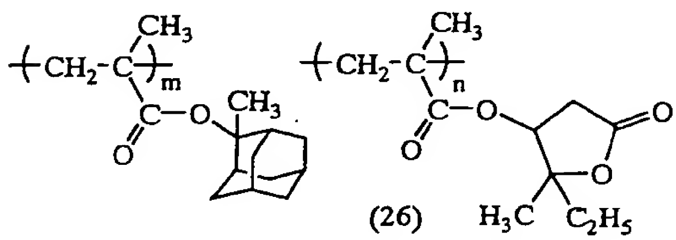

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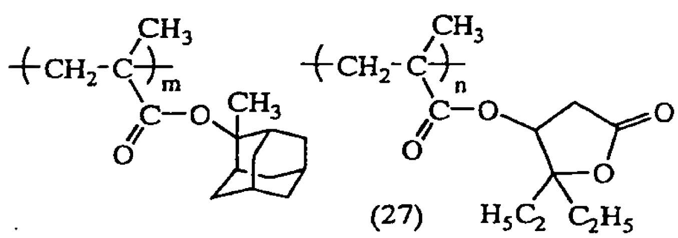

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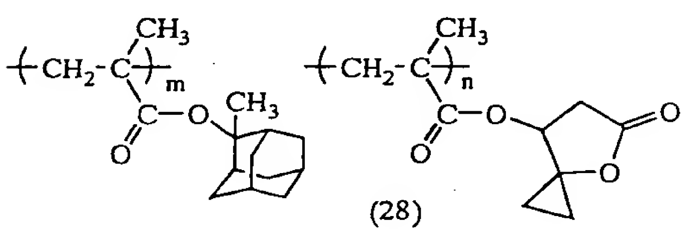

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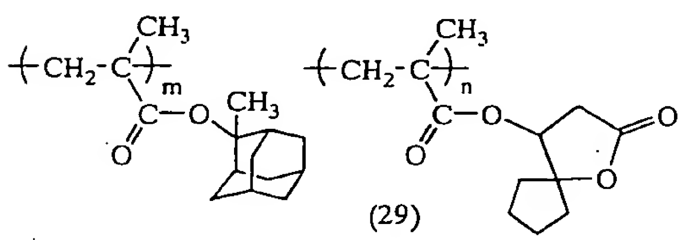

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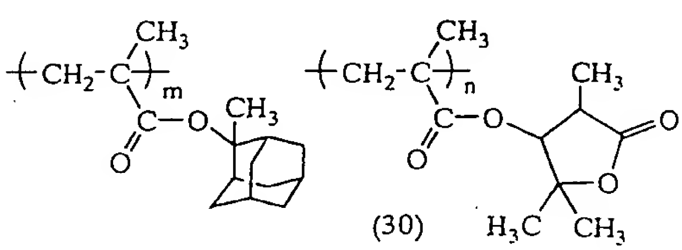

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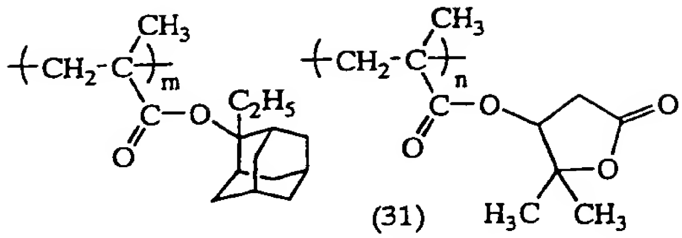

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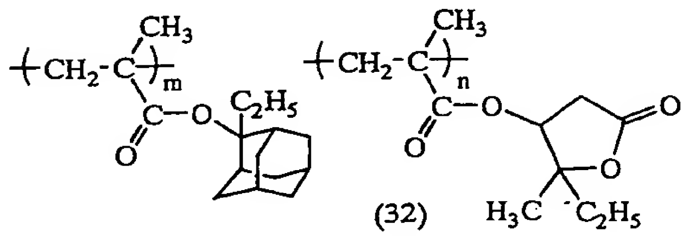

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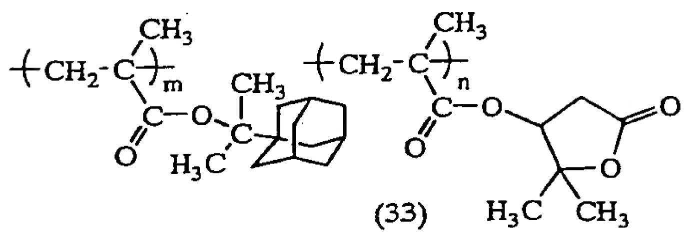

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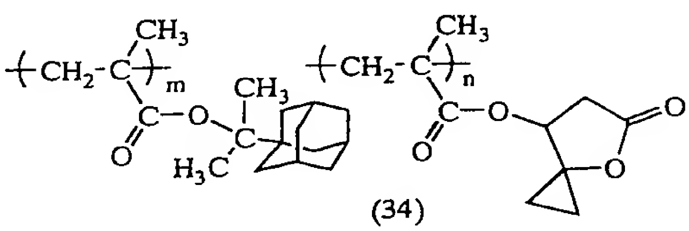

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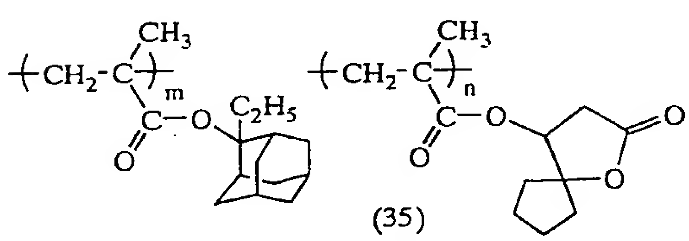

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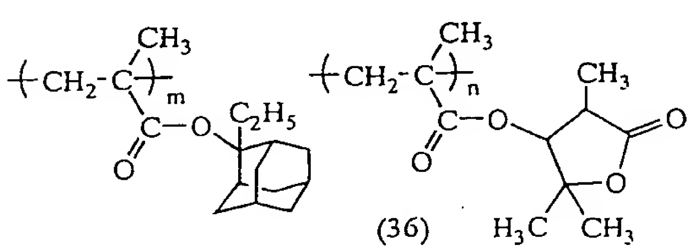

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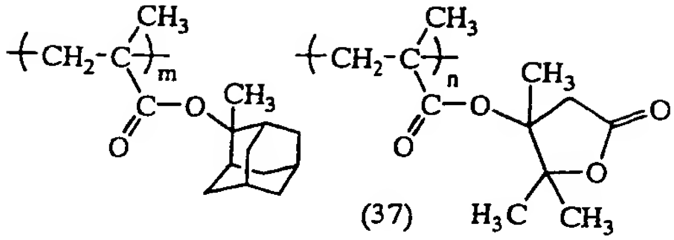

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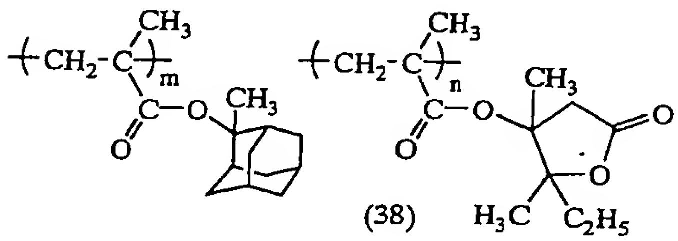

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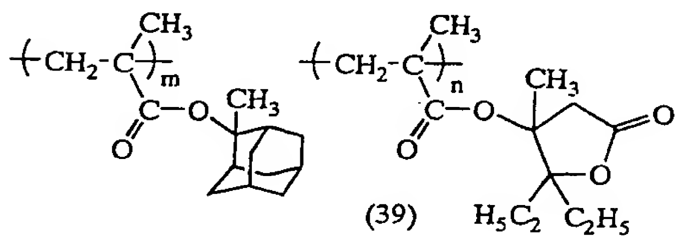

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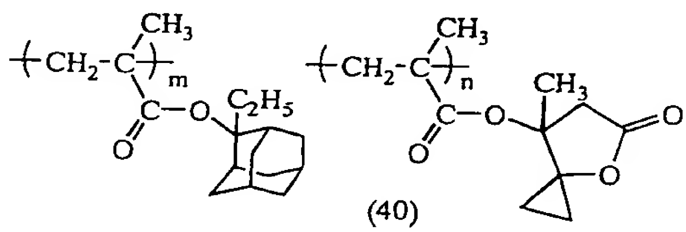

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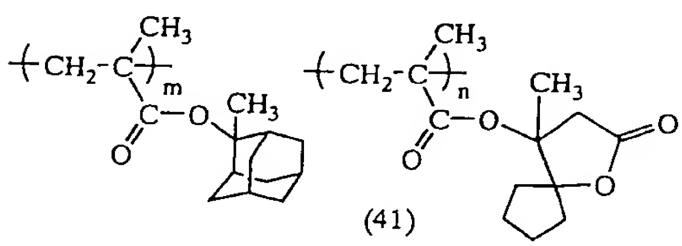

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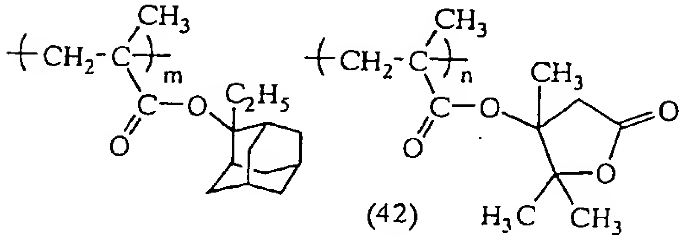

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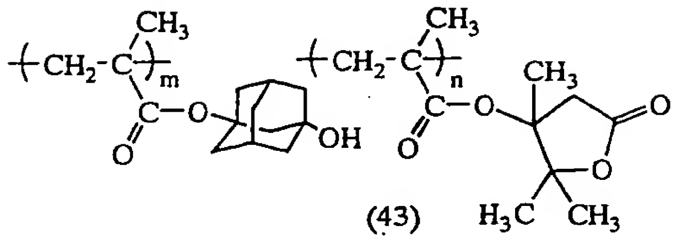

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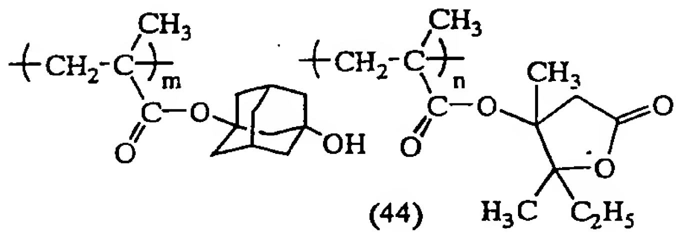

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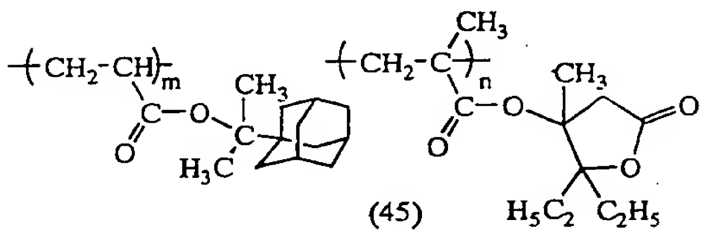

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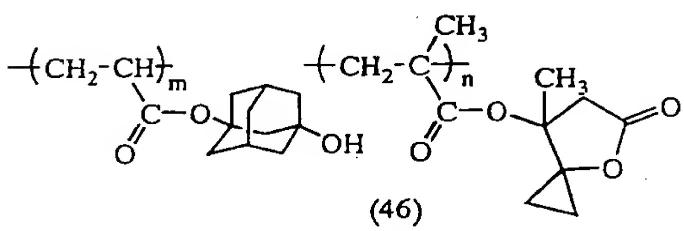

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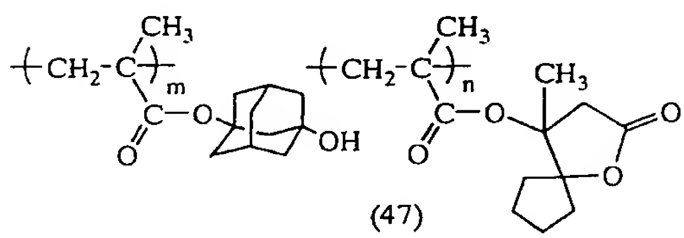

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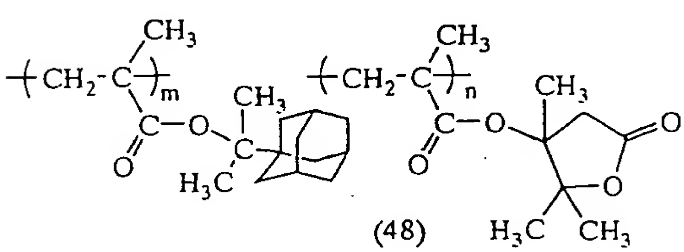

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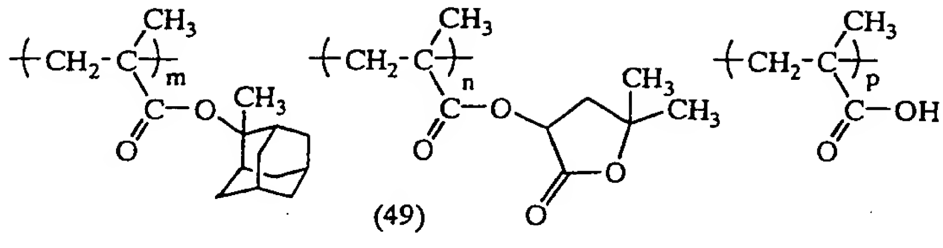

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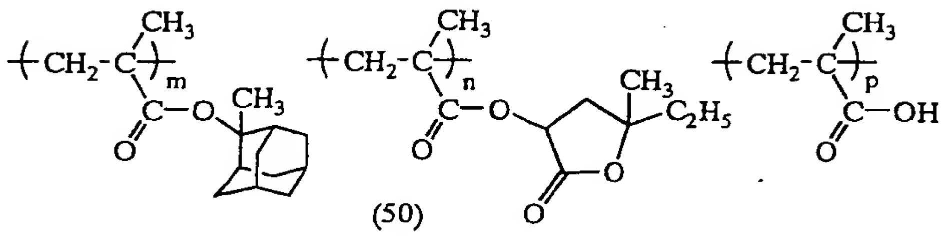

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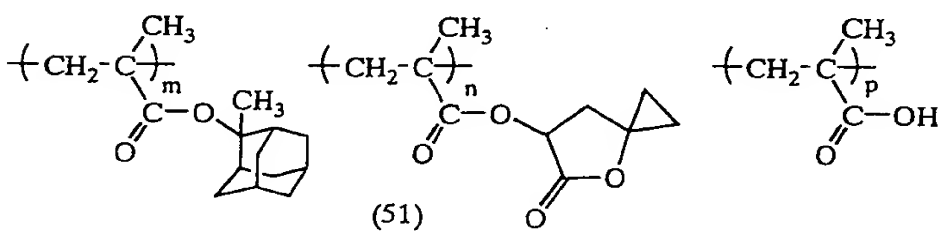

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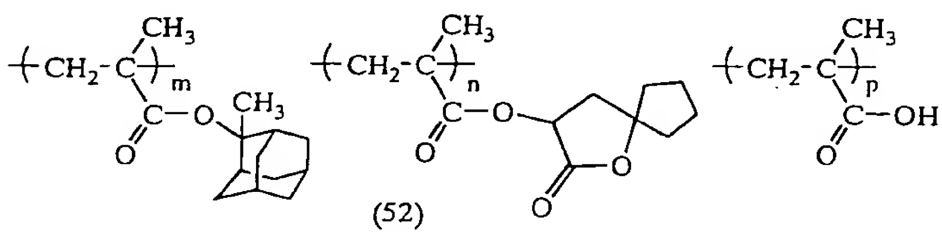

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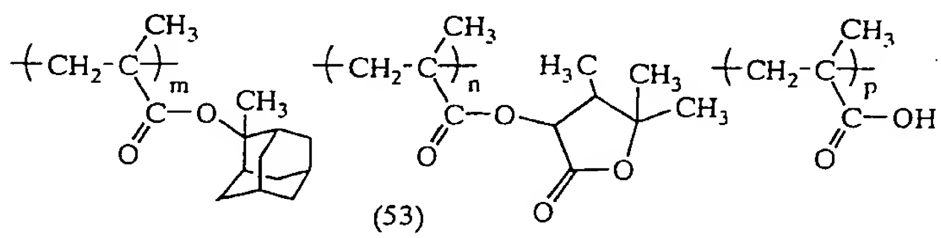

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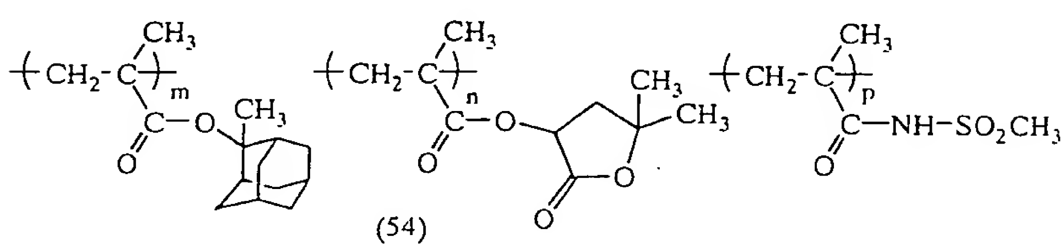

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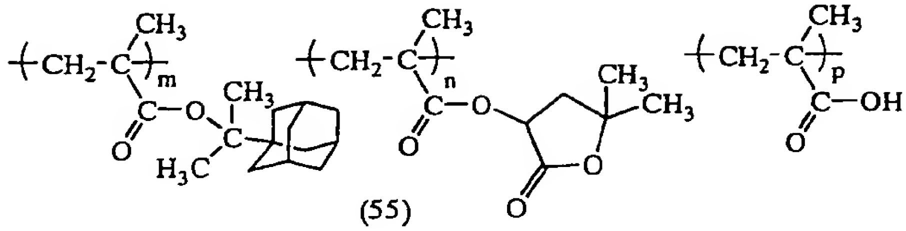

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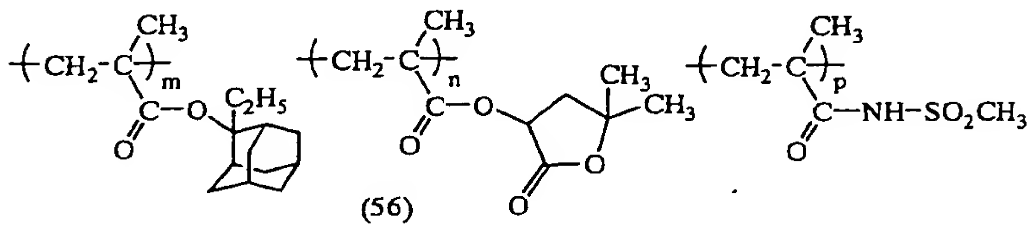

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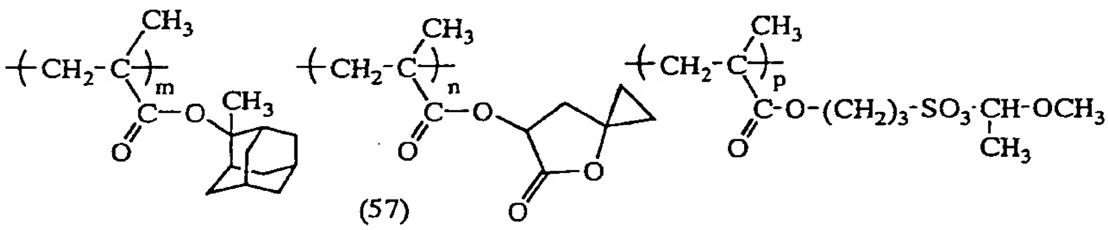

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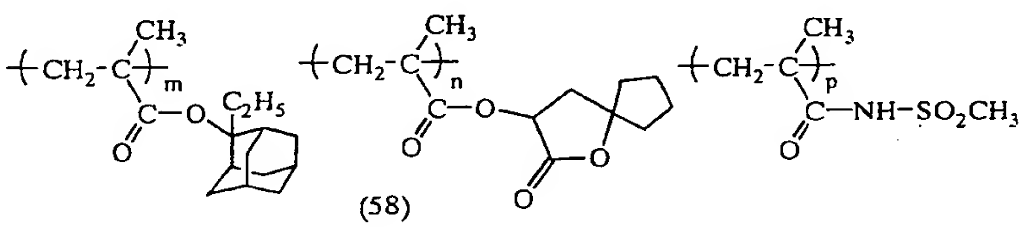

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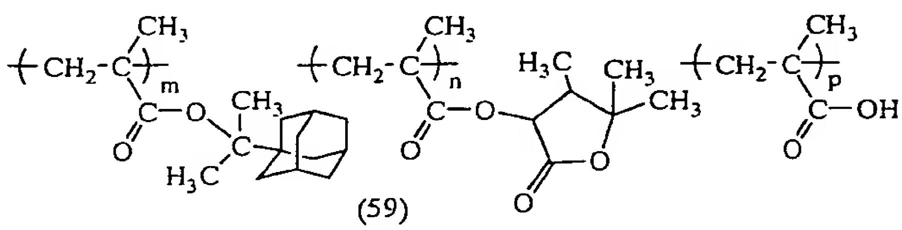

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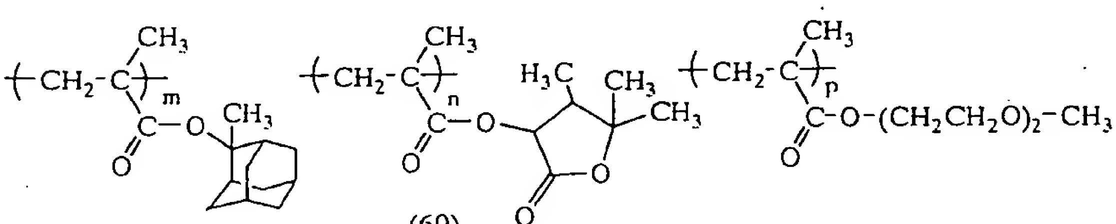

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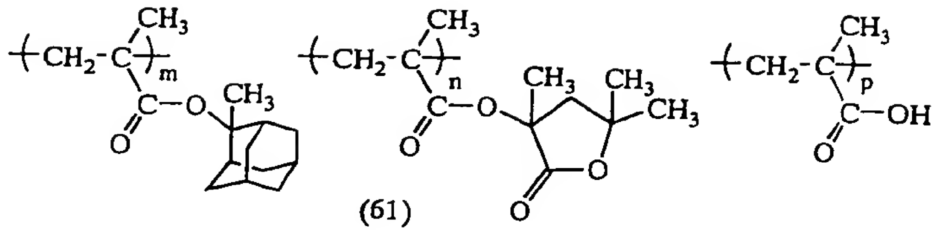

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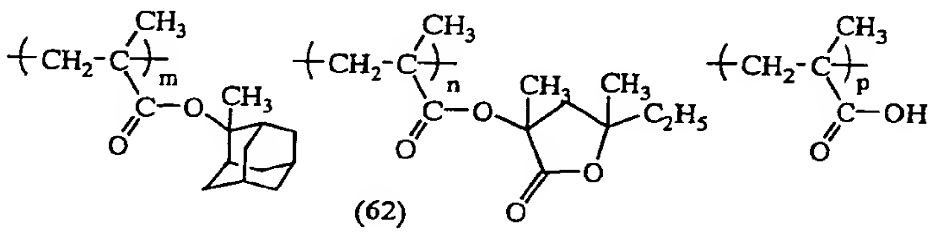

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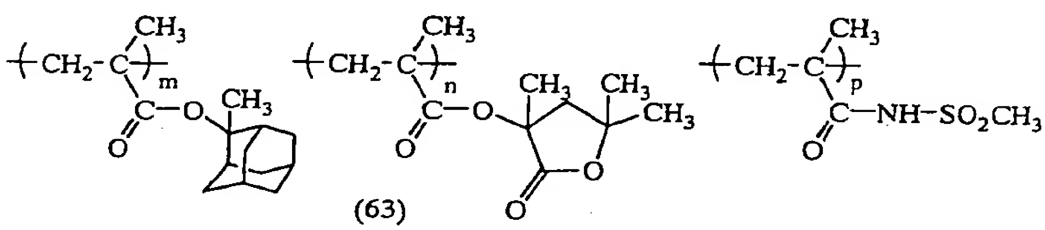

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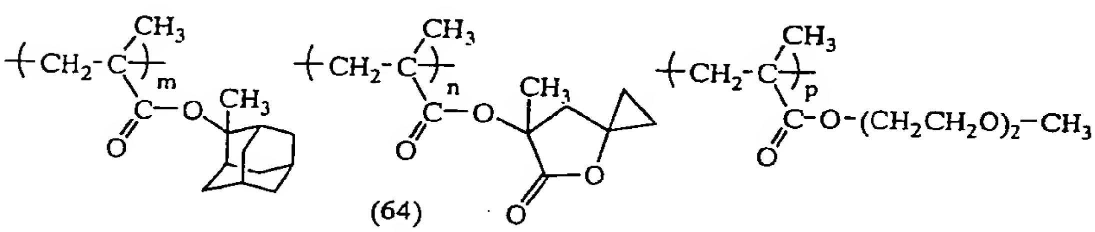

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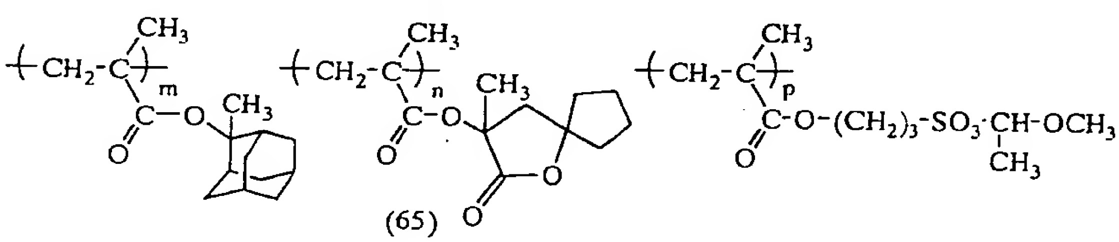

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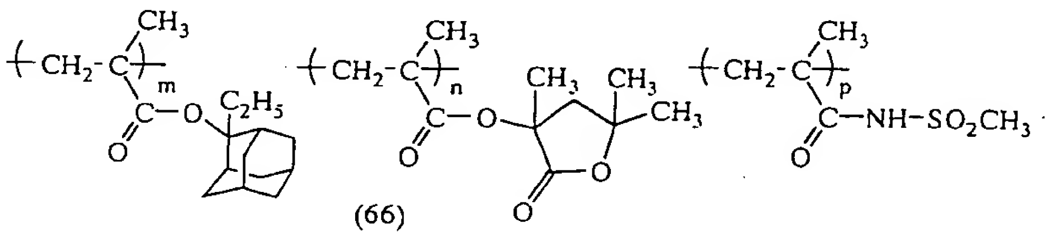

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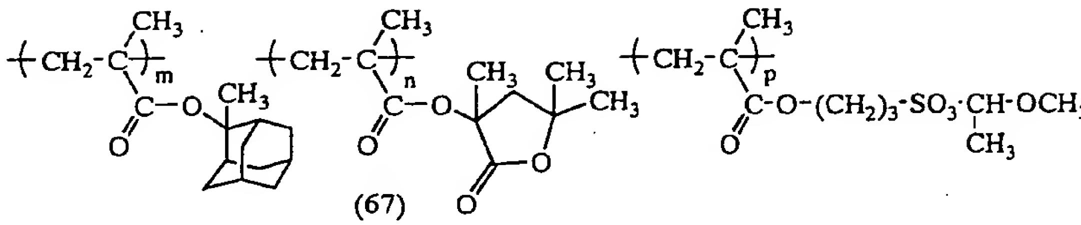

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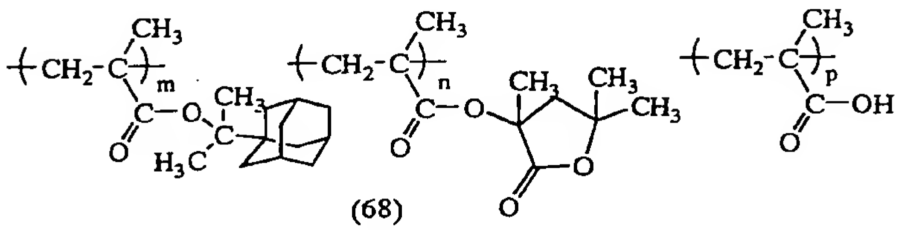

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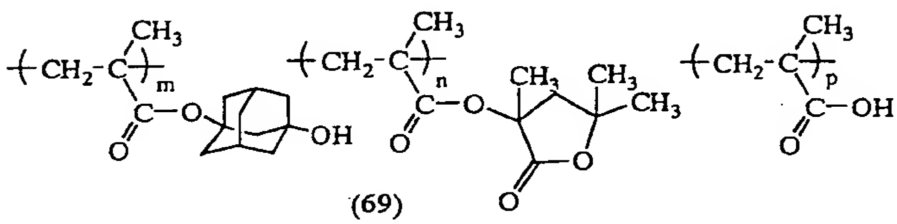

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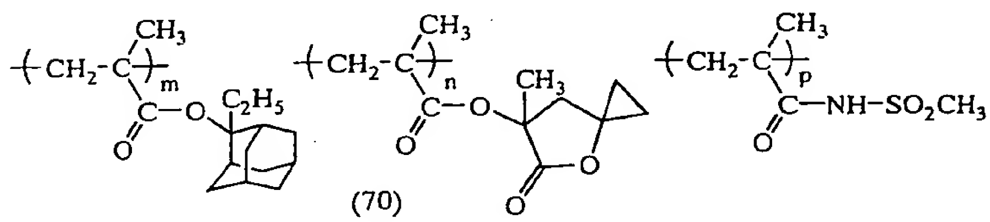

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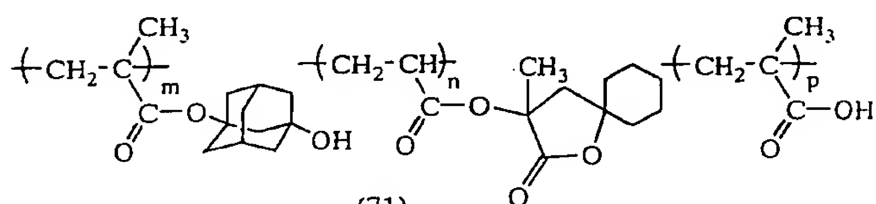

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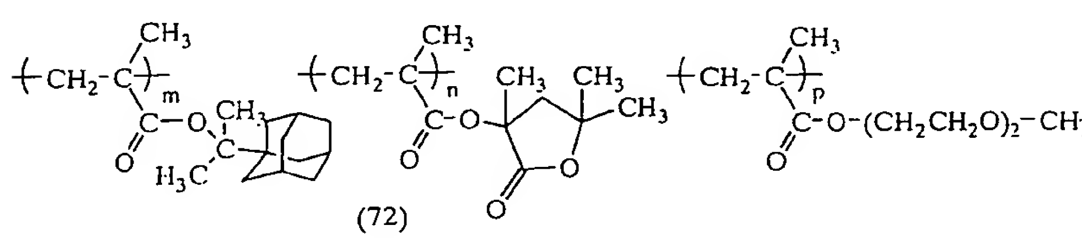

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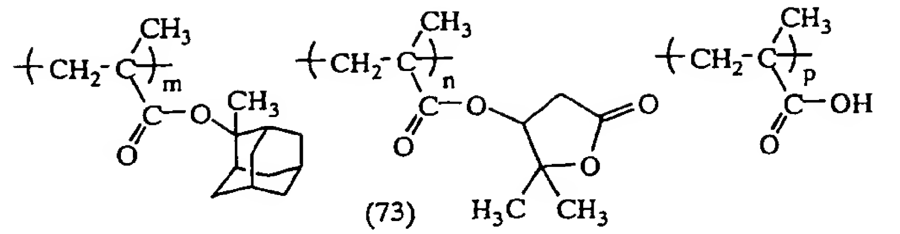

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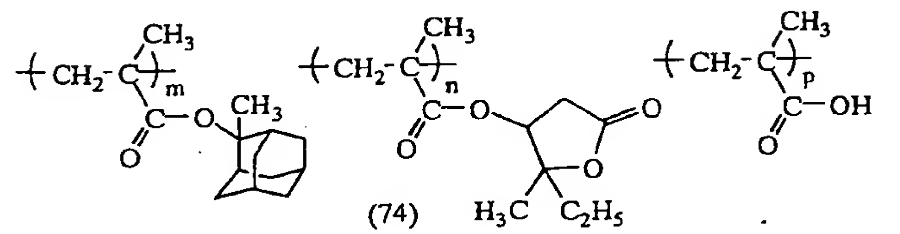

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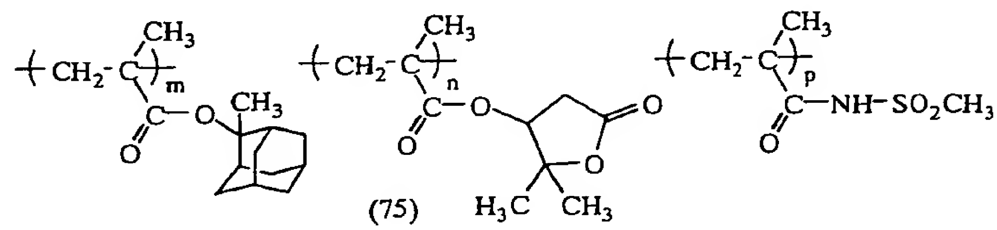

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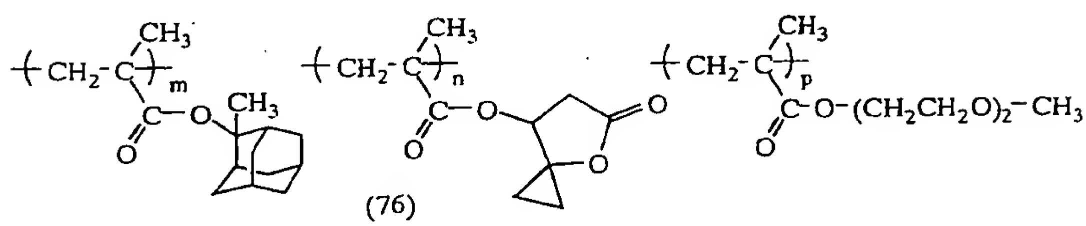

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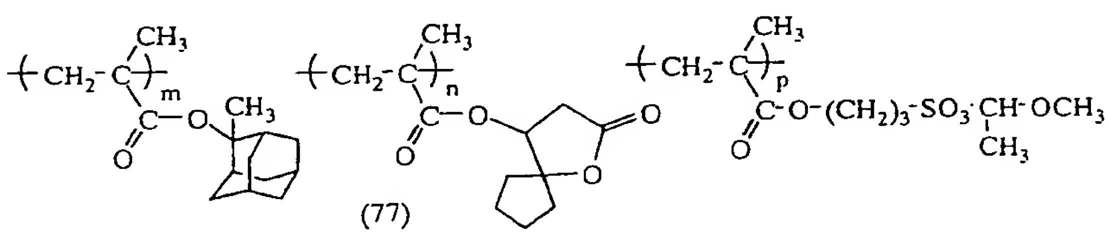

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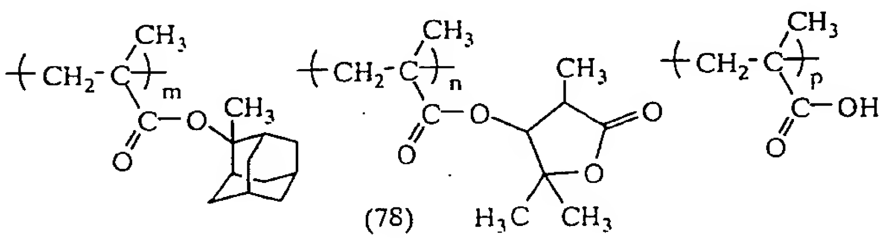

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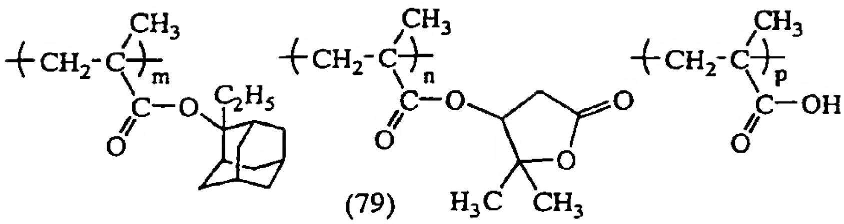

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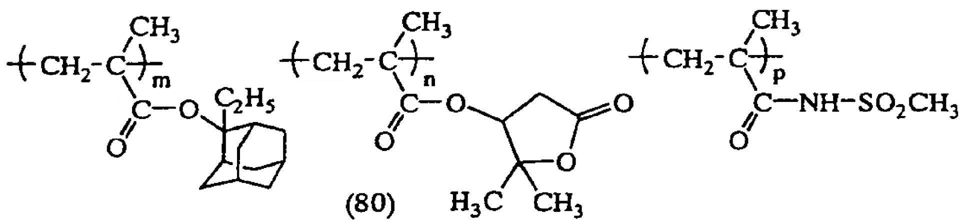

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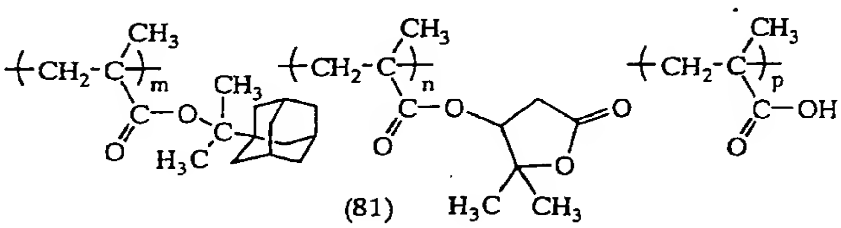

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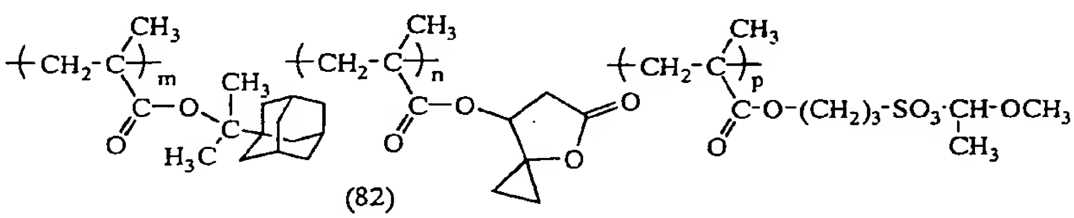

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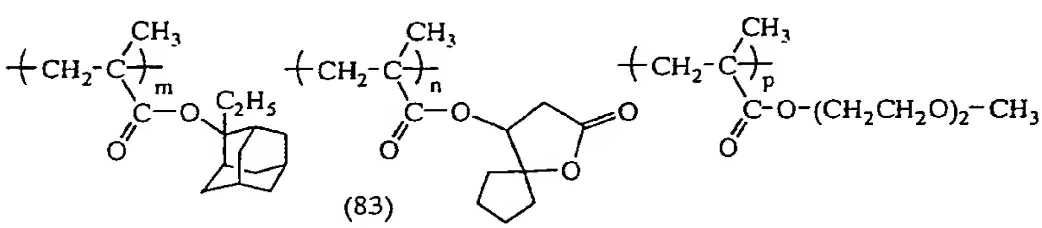

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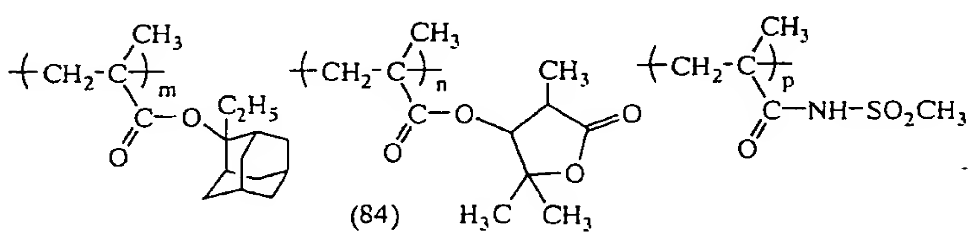

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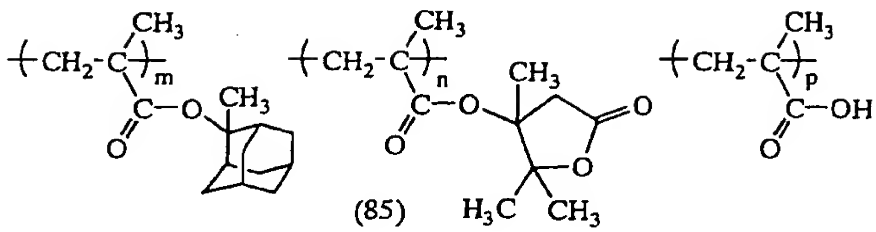

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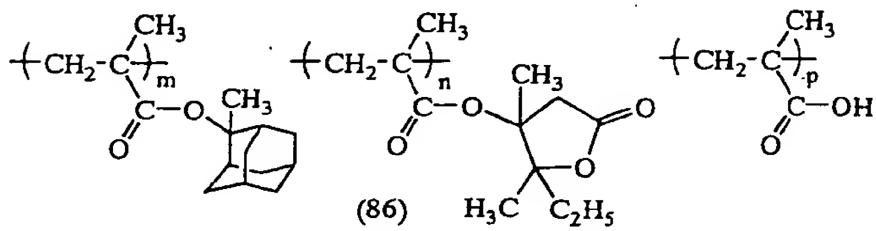

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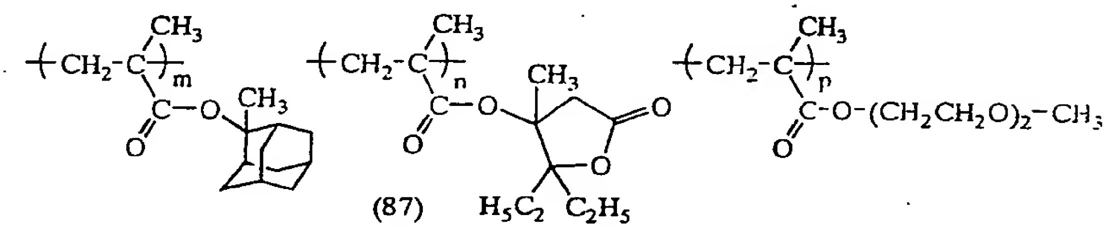

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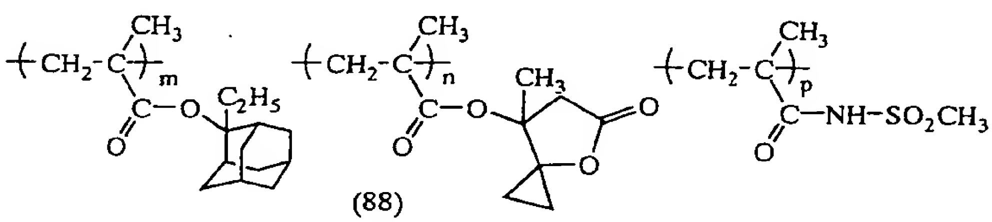

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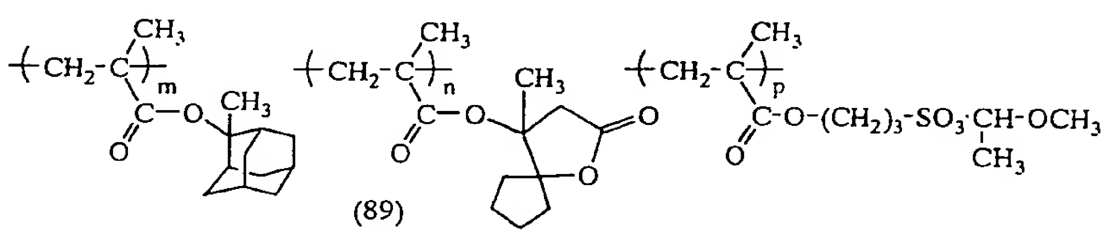

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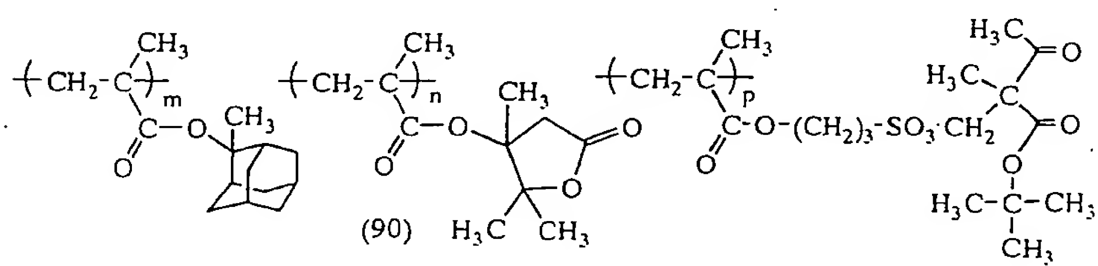

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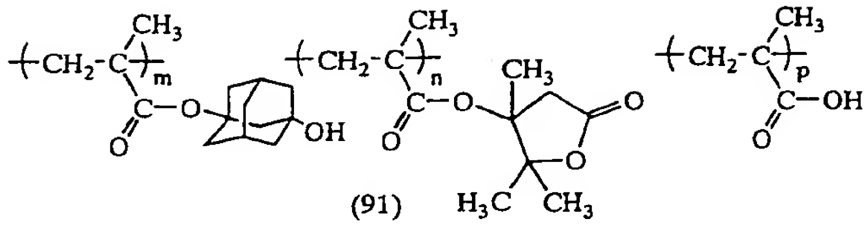

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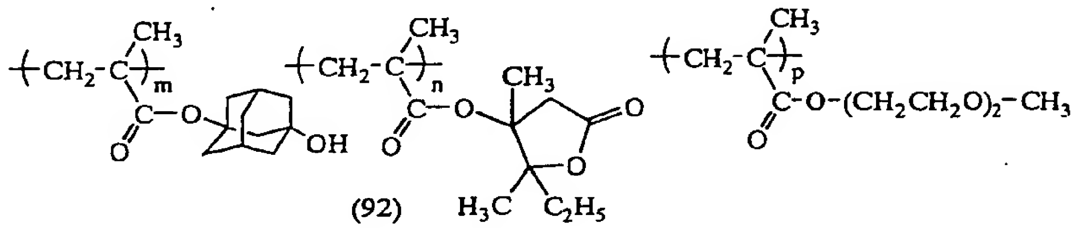

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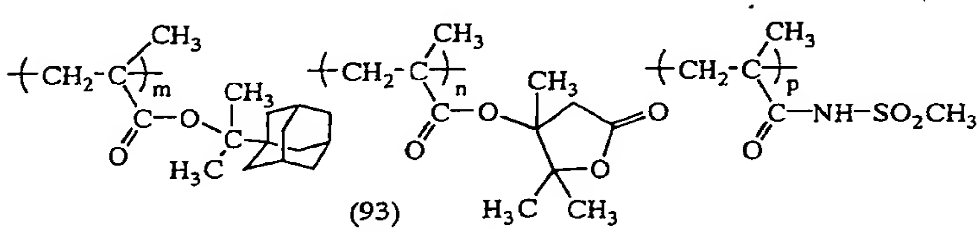

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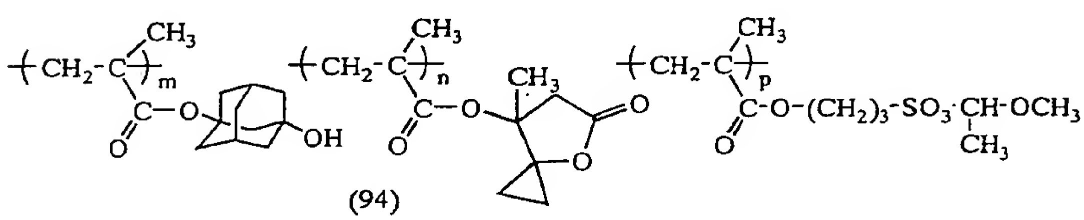

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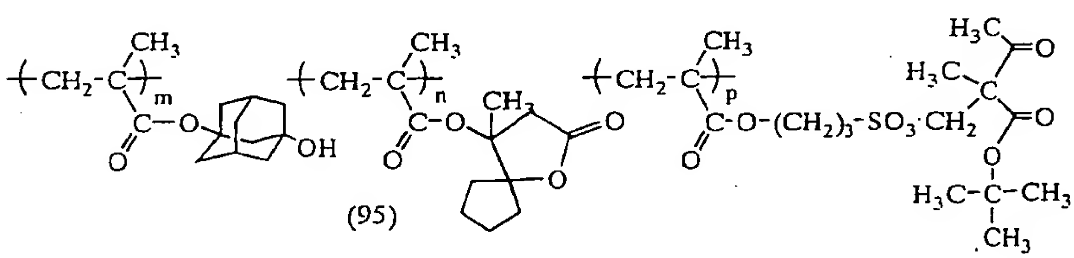

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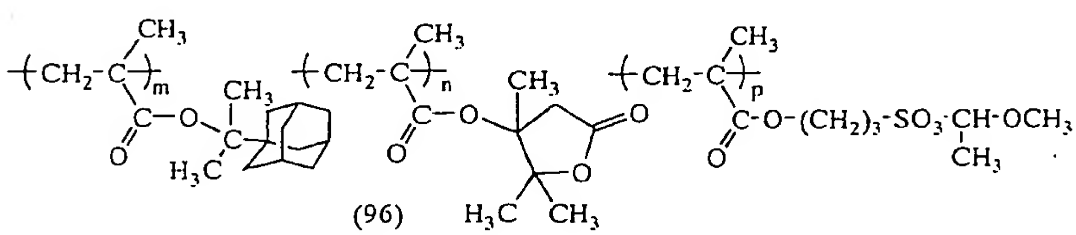


(96)

In the positive photoresist composition for far ultraviolet exposure of the present invention, the amount of the resin (B) added in the entire composition is preferably from 40 to 99.99 wt%, more preferably from 50 to 99.97 wt%, based on all solid contents in the resist.

The positive resist composition of the present invention may further contain, if desired, an acid-decomposable dissolution inhibiting compound, a dye, a plasticizer, a surfactant, a photosensitizer, an organic basic compound and a compound capable of accelerating the dissolution in a developer.

The positive photoresist composition of the present invention may contain a fluorine-containing surfactant and/or a silicon-containing surfactant.

The positive photoresist composition of the present invention may contain one or more of a fluorine-containing surfactant, a silicon-containing surfactant and a surfactant containing both fluorine atom and silicon atom.

Examples of the surfactant include surfactants described in JP-A-62-36663, JP-A-61-226746, JP-A-61-226745, JP-A-62-170950, JP-A-63-34540, JP-A-7-230165, JP-A-8-62834, JP-A-9-54432 and JP-A-9-5988. Also, the commercially available surfactants described below each may be used as it is.

Examples of the commercially available surfactants which can be used include fluorine-containing surfactants and silicon-containing surfactants, such as Eftop EF301 and EF303 (produced by Shin-Akita Kasei K.K.), Florad FC430 and 431 (produced by Sumitomo 3M Inc.), Megafac F171, F173, F176, F189 and R08 (produced by Dainippon Ink & Chemicals, Inc.), and Surflon S-382, SC101, 102, 103, 104, 105 and 106 (produced by Asahi Glass Co., Ltd.). Also, a polysiloxane polymer KP-341 (produced by Shin-Etsu Chemical Co., Ltd.) may be used as a silicon-containing surfactant.

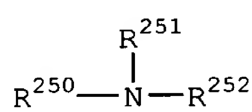
The amount of the surfactant blended is usually from 0.001 to 2 wt%, preferably from 0.01 to 1 wt%, based on the solid content in the composition of the present invention. These surfactants may be used either individually or in combination.

Specific examples of other surfactants which can be used include nonionic surfactants including polyoxyethylene alkyl ethers such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene cetyl ether and polyoxyethylene oleyl ether; polyoxyethylene alkyl aryl ethers such as polyoxyethylene octyl phenol ether and polyoxyethylene nonyl phenol ether; polyoxy-ethylene/polyoxypropylene block copolymers; sorbitan fatty acid esters such as sorbitan monolaurate, sorbitan

monopalmitate, sorbitan monostearate, sorbitan monooleate, sorbitan trioleate and sorbitan tristearate; and polyoxyethylene sorbitan fatty acid esters such as polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan trioleate and polyoxyethylene sorbitan tristearate.

The amount of this surfactant blended is usually 2 parts by weight or less, preferably 1 part by weight or less, per 100 parts by weight of the solid content in the composition of the present invention.

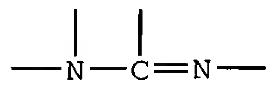
The acid diffusion inhibitor (C) for use in the present invention is preferably added so as to inhibit the fluctuation of sensitivity and resolution in aging from the exposure until heating and development. This is preferably an organic basic compound. Examples of the organic basic compound include a nitrogen-containing basic compound having the following structure:



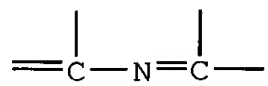
(A)

wherein R^{250}, R^{251} and R^{252}, which may be the same or different, each represents hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, an aminoalkyl group having from 1 to 6 carbon atoms, a hydroxyalkyl group having from

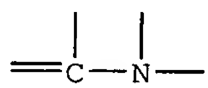
1 to 6 carbon atoms or a substituted or unsubstituted aryl group having from 6 to 20 carbon atoms, or R^{251} and R^{252} may be combined with each other to form a ring.



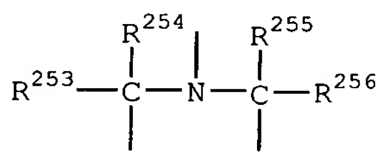
(B)



(C)



(D)



(E)

(wherein R^{253}, R^{254}, R^{255} and R^{256}, which may be the same or different, each represents an alkyl group having from 1 to 6 carbon atoms).

The compound is more preferably a nitrogen-containing basic compound having two or more nitrogen atoms different in the chemical environment within one molecule, still more preferably a compound having both a substituted or unsubstituted amino group and a ring structure containing nitrogen atom or a compound having an alkylamino group. Specific preferred examples thereof include substituted or unsubstituted guanidine, substituted or unsubstituted aminopyridine, substituted or unsubstituted aminoalkyl-pyridine, substituted or unsubstituted aminopyrrolidine,

substituted or unsubstituted indazole, substituted or unsubstituted pyrazole, substituted or unsubstituted pyrazine, substituted or unsubstituted pyrimidine, substituted or unsubstituted purine, substituted or unsubstituted imidazoline, substituted or unsubstituted pyrazoline, substituted or unsubstituted piperazine, substituted or unsubstituted aminomorpholine and substituted or unsubstituted aminoalkylmorpholine. Preferred examples of the substituent include an amino group, an aminoalkyl group, an alkylamino group, an aminoaryl group, an arylamino group, an alkyl group, an alkoxy group, an acyl group, an acyloxy group, an aryl group, an aryloxy group, a nitro group, a hydroxyl group and a cyano group.

Specific examples of preferred compounds include guanidine, 1,1-dimethylguanidine, 1,1,3,3-tetramethylguanidine, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylaminopyridine, 4-dimethylaminopyridine, 2-diethylaminopyridine, 2-(aminomethyl)pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethylpyridine, 4-aminoethylpyridine, 3-aminopyrrolidine, piperazine, N-(2-aminoethyl)piperazine, N-(2-aminoethyl)-piperidine, 4-amino-2,2,6,6-tetramethylpiperidine, 4-

piperidinopiperidine, 2-iminopiperidine, 1-(2-aminoethyl)-pyrrolidine, pyrazole, 3-amino-5-methylpyrazole, 5-amino-3-methyl-1-p-tolylpyrazole, pyrazine, 2-(aminomethyl)-5-methylpyrazine, pyrimidine, 2,4-diaminopyrimidine, 4,6-dihydroxypyrimidine, 2-pyrazoline, 3-pyrazoline, N-amino-morpholine, N-(2-aminoethyl)morpholine, 1,5-diaza-bicyclo[4.3.0]-5-nonene, 1,8-diazabicyclo[5.4.0]-7-undecene, 2,4,5-triphenylimidazole, N-methylmorpholine, N-ethyl-morpholine, N-hydroxyethylmorpholine, N-benzylmorpholine, tertiary morpholine derivatives such as cyclohexyl-morpholinoethylthiourea (CHMETU), and hindered amines described in JP-A-11-52575 (for example, those described in [0005] of this patent publication), however, the present invention is by no means limited thereto.

Specific examples of more preferred compounds include 1,5-diazabicyclo[4.3.0]-5-nonene, 1,8-diazabicyclo[5.4.0]-7-undecene, 1,4-diazabicyclo[2.2.2]octane, 4-dimethylamino-pyridine, hexamethylenetetramine, 4,4-dimethylimidazoline, pyrroles, pyrazoles, imidazoles, pyridazines, pyrimidines, tertiary morpholines such as CHMETU, and hindered amines such as bis(1,2,2,6,6-pentamethyl-4-pyperidyl) sebacate.

Among these compounds, 1,5-diazabicyclo[4.3.0]-5-nonene, 1,8-diazabicyclo[5.4.0]-7-undecene, 1,4-diazabicyclo[2.2.2]octane, 4-dimethylaminopyridine,

hexamethylenetetramine, CHMETU and bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate are preferred.

These nitrogen-containing basic compounds may be used either individually or in combination of two or more thereof. The amount of the nitrogen-containing basic compound used is usually from 0.001 to 10 wt%, preferably from 0.01 to 5 wt%, based on the solid content of the entire photosensitive resin composition. If the amount used is less than 0.001 wt%, the effect resulting from the addition of the nitrogen-containing basic compound may not be obtained, whereas if it exceeds 10 wt%, the sensitivity is liable to decrease or the developability in the unexposed area is readily worsened.

The positive resist composition of the present invention is dissolved in a solvent capable of dissolving the above-described components and then coated on a support. The solvent used here is preferably ethylene dichloride, cyclohexanone, cyclopentanone, 2-heptanone, γ-butyrolactone, methyl ethyl ketone, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxyethyl acetate, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, toluene, ethyl acetate, methyl lactate, ethyl lactate, methyl methoxypropionate, ethyl ethoxypropionate, methyl

pyruvate, ethyl pyruvate, propyl pyruvate, N,N-dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone or tetrahydrofuran. These solvents are used individually or in combination.

Among these solvents, preferred are 2-heptanone, γ-butyrolactone, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether, propylene glycol monoethyl ether, methyl lactate, ethyl lactate, methyl methoxypropionate, ethyl ethoxypropionate, N-methylpyrrolidone and tetrahydrofuran.

The thus-prepared positive resist composition of the present invention is coated on a substrate to form a thin film. The coated film preferably has a thickness of 0.2 to 1.2 μm. In the present invention, if desired, a commercially available inorganic or organic anti reflection coating may be used.

Examples of the anti reflection coating which can be used include the inorganic film type such as titanium, titanium dioxide, titanium nitride, chromium oxide, carbon and α-silicon, and the organic film type comprising a light absorbent and a polymer material. In the former case, equipment such as vacuum evaporation apparatus, CVD apparatus and sputtering apparatus is necessary for the

film formation. Examples of the organic anti reflection coating include a film comprising a condensation product of a diphenylamine derivative and a formaldehyde-modified melamine resin, an alkali-soluble resin and a light absorbent described in JP-B-7-69611, a reactant of a maleic acid anhydride copolymer and a diamine-type light absorbent described in U.S. Patent 5,294,680, a film containing a resin binder and a methylol melamine-base heat cross-linking agent described in JP-A-6-118631, an acrylic resin-type anti reflection coating having a carboxylic acid group, an epoxy group and a light-absorbing group within the same molecule described in JP-A-6-118656, a film comprising methylolmelamine and a benzophenone-base light absorbent described in JP-A-8-87115, and a polyvinyl alcohol resin having added thereto a low-molecular weight light absorbent described in JP-A-8-179509.

In addition, organic anti reflection coating such as DUV30 series and DUV-40 series produced by Brewer Science, and AC-2 and AC-3 produced by Shipley may also be used.

The resist solution is coated on a substrate (for example, silicon/silicon dioxide coating), and (if desired, after providing the above-described anti reflection coating on the substrate) used in the production of precision integrated circuit devices by an appropriate coating method

such as spinner and coater, exposed through a predetermined mask, baked and developed, whereby a good resist pattern can be obtained. The exposure light used here is preferably light at a wavelength of 150 to 250 nm. More specifically, a KrF excimer laser (248 nm), an ArF excimer laser (193 nm), an F_2 excimer laser (157 nm), an X ray, an electron beam and the like may be used.

The developer which can be used is an alkaline aqueous solution of an inorganic alkali such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate and aqueous ammonia, a primary amine such as ethylamine and n-propylamine, a secondary amine such as diethylamine and di-n-butylamine, a tertiary amine such as triethylamine and methyldiethylamine, an alcohol-amine such as dimetylethanolamine and triethanolamine, a quaternary ammonium salt such as tetramethylammonium hydroxide and tetraethylammonium hydroxide, and a cyclic amine such as pyrrole and piperidine.

Furthermore, to this alkaline aqueous solution, an alcohol and a surfactant may be added each in an appropriate amount.

[Example]

The present invention is described in greater detail

below by referring to the Examples, however, the present invention should not be construed as being limited thereto.

SYNTHESIS EXAMPLE (1)

Synthesis of Resin (1) of the present invention:

2-Methyl-2-adamantyl methacrylate and 4,4-dimethyl-2-γ-butyrolactone methacrylate were charged in a molar ratio of 50/50 and dissolved in N,N-dimethylacetamide/tetrahydrofuran (5/5) to prepare 100 ml of a solution having a solid concentration of 20%. To this solution, 3 mol% of V-65 produced by Wako Pure Chemical Industries, Ltd. was added and the resulting solution was added dropwise to 10 ml of N,N-dimethylacetamide heated at 60°C, over 3 hours in a nitrogen atmosphere. After the completion of dropwise addition, the reaction solution was heated for 3 hours and again, 1 mol% of V-65 was added, followed by stirring for 3 hours. After the completion of reaction, the reaction solution was cooled to room temperature and crystallized with 3 liter of distilled water and the white powder precipitated was recovered.

The polymer compositional ratio determined by C^{13} NMR was 52/48. The weight-average molecular weight in terms of the standard polystyrene determined by GPC was 8,200.

SYNTHESIS EXAMPLES 2 TO 16

Synthesis of Resins (2) to (16) of the present invention:

Resins 2 to 16 each having a compositional ratio and a weight-average molecular weight shown in Table 1 below were synthesized in the same manner as in Synthesis Example 1 above.

TABLE 1

Synthesis Example	Resin of the Invention (Resin No.)	Compositional Ratio (by mol), m/n or m/n/p	Molecular Weight
2	(2)	51/49	7,500
3	(5)	53/47	9,600
4	(8)	50/50	6,400
5	(13)	51/49	8,400
6	(21)	54/46	10,300
7	(31)	52/48	8,800
8	(42)	51/49	10,500
9	(49)	47/45/8	8,900
10	(55)	49/42/9	9,200
11	(61)	48/42/10	7,900
12	(65)	50/43/7	8,300
13	(66)	44/44/12	10,900
14	(69)	43/47/10	8,700
15	(85)	45/45/10	9,200
16	(95)	47/45/8	7,800

EXAMPLES 1 TO 16

[Preparation and Evaluation of Photosensitive Compositions]

1.4 g of the resin synthesized in Synthesis Examples

above and 0.2 g of a photo-acid generator were mixed and dissolved in propylene glycol monomethyl ether acetate each to a concentration of 14 wt% as the solid content. The resulting solution was filtered through a 0.1-μm microfilter to prepare positive resists of Examples 1 to 16. The resins of the present invention and the photoacid-generators used are shown in Table 2 below.

Separately, a positive resist for comparison was prepared using Resin (A4) synthesized in the same manner as in the synthesis described at page 8 of JP-A-10-274852.

(Evaluation Test)

The thus-obtained positive photoresist solutions each was coated on a silicon wafer using a spin coater and dried at 130°C for 90 seconds to form a positive photoresist film having a thickness of about 0.4 μm. The resist film formed was exposed by an ArF excimer laser (exposed by an ArF stepper at a wavelength of 193 nm with NA=0.6, manufactured by ISI), heat-treated at 120°C for 90 seconds, developed with an aqueous 2.38% tetramethylammonium hydroxide solution and rinsed with distilled water to obtain a resist pattern profile.

These were evaluated as follows on the sensitivity, resolution and edge roughness. The evaluation results are shown in Table 2.

[Sensitivity]

The sensitivity was evaluated by the minimum exposure amount necessary for reproducing a 0.15-μm line-and-space pattern.

[Resolution]

The resolution was evaluated by the limiting resolution which can be reproduced with the minimum exposure amount for reproducing a 0.15-μm line-and-space pattern.

[Edge Roughness]

The edge roughness was measured for the edge roughness of an isolated pattern using a critical dimension scanning electron microscope (SEM). The line pattern edge was detected at a plurality of positions within the measuring monitor and the dispersion (3σ) of the detected positions was used as an index for edge roughness. The smaller value is more preferred.

TABLE 2

Examples	Resin of the Invention	Photo-Acid Generator	Sensitivity (mJ/cm^2)	Resolution (μm)	Edge Roughness (nm)
1	(1)	PAG4-5	19	0.13	12
2	(2)	PAG4-5	17	0.13	11
3	(5)	PAG3-23	20	0.13	12
4	(8)	PAG4-5	13	0.13	13
5	(13)	PAG4-7	12	0.13	10
6	(21)	PAG3-23	21	0.13	11
7	(31)	PAG4-5	18	0.13	12
8	(42)	PAG7-4	20	0.13	13
9	(49)	PAG4-5	17	0.13	14
10	(55)	PAG3-23	22	0.14	12
11	(61)	PAG3-22	9	0.13	11
12	(65)	PAG6-19	19	0.14	10
13	(66)	PAG7-4	17	0.13	13
14	(69)	PAG3-23	19	0.13	14
15	(85)	PAG4-5	12	0.13	12
16	(95)	PAG4-5	14	0.14	11
Comparative Example	(A4)	PAG4-5	32	0.15	28

As apparent from the results in Table 2, the positive resist compositions of the present invention are all in a satisfactory level, namely, they are suitable for the lithography using a far ultraviolet ray as in the ArF excimer laser exposure.

[Advantage of the Invention]

The present invention can provide a positive resist composition suitable of a far ultraviolet ray, particularly

an ArF excimer laser ray, excellent in the sensitivity, resolution and edge roughness, and capable of providing an excellent resist pattern profile.

[Name of Document] Summary

[Summary]

[Object] To provide an excellent chemical amplification-system positive photoresist composition having high sensitivity and high resolution and improved in edge roughness of pattern.

[Means to resolve the Problem] A positive photoresist composition comprising a compound capable of generating an acid upon irradiation with actinic rays or radiation and a resin capable of decomposing under the action of an acid to increase the solubility in alkali, containing a repeating unit including a specific structure.

[Selected Drawing] None